

PHOTOPHYSICS OF PI-CONJUGATED POLYMERS AND OLIGOMERS THAT
INCORPORATE METAL TO LIGAND CHARGE TRANSFER CHROMOPHORES

By

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Dedicated to Aunt Sara, whose heart and generosity are without equal

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PHOTOPHYSICS OF π I-CONJUGATED POLYMERS AND OLIGOMERS THAT
INCORPORATE METAL TO LIGAND CHARGE TRANSFER CHROMOPHORES

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The field of conjugated polymers has seen explosive growth in the past ten years, with applications for these polymers ranging from polymer-based LED devices to molecular electronics. Although considerable attention has focused on all organic π -conjugated polymers, considerably less work has focused on their metal-organic counterparts. This is surprising seeing that many transition metals feature intense metal-to-ligand charge transfer (MLCT) transitions that are ligand tunable. Incorporation of a transition metal MLCT chromophore within a π -conjugated polymer might allow one to custom tune the optical properties of the polymer. With this in mind, the synthesis and

optical characterization of a series of PPE (poly(phenyleneethynylene)) polymers and oligomers that incorporate MLCT chromophores are presented.

A series of poly(phenyleneethynylene) π -conjugated polymers incorporating a *fac*-(5,5'-diethynyl-2,2'-bipyridine) $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}$ chromophore were synthesized by palladium-mediated coupling chemistry. One organic and three metal-organic polymers **P0**, **P10**, **P25** and **P50** have been prepared which contain, respectively, 0, 10, 25 and 50 mole % of the $\text{Re}(\text{I})$ repeat units in the polymer chain. The metal-organic polymers feature two spectrally-distinct absorption bands, both of π, π^* nature. The luminescence properties of these polymers were examined in fluid solution and in a 2-methyltetrahydrofuran glass. These spectroscopic studies reveal that fluorescence from the π, π^* exciton state is observed in all polymers; in addition, phosphorescence from the $^3\pi, \pi^*$ state of the conjugated polymer backbone and luminescence from the $d\pi \rightarrow \pi^*$ MLCT state is observed.

To gain a further understanding of the optical properties of polymers **P0** – **P50**, a series of poly(phenyleneethynylene) oligomers, were synthesized with the *fac*- $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}$ chromophore incorporated via a 2,2'-bipyridyl unit. Unlike the previously synthesized polymers, these oligomers have well defined repeat structures, allowing for the development of structure-photophysical property relationships. The photophysical studies of these compounds provided a wealth of knowledge in regard to the effects of metal-coordination to the oligomer backbone, the relative conjugation length of the oligomer as a function of polymer backbone structure, as well as the effect that the extended conjugation has on the energies of the $^3\pi, \pi^*$ and $^3\text{MLCT}$ excited states.

CHAPTER 1

INTRODUCTION

π -Conjugated Polymers and Oligomers

The research area of π -conjugated polymers has seen tremendous growth in the past 10 years [1-15]. The interest in these polymers revolves around their possible applications towards chemical sensors [1,2] and molecular electronic devices [16,17]. Some of the properties of these polymers that account for their desirability are their large fluorescence quantum yields [18], non-linear optical properties [19,20] and semi-conductive properties [21-23]. Three major classes of fluorescent π -conjugated polymers are polyphenylene (PPP), polyphenylvinylene (PPV) and polyphenyleneethynylene (PPE) (Figure 1.1)

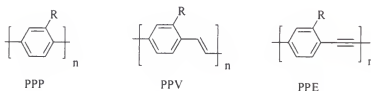


Figure 1.1: Three classes of π -conjugated polymers.

Polyphenyleneethynylene

The conjugated polymers that have received the most interest are undoubtedly the PPP and PPV derivatives. The interest in these polymers is associated with their application as the organic component in LED based devices [23-32]. Although the PPE based polymers have received considerable attention

in the last few years, they still are largely overshadowed by their PPP and PPV counterparts. In the past few years, the research by Swager, Weder, and Mullen showed the direct application of PPE polymers in explosive detection [33], molecular wires in bridging nanogaps [34,35] as well as polarizers for LC devices [12]. These individuals not only found significant uses for these polymers, but also pioneered the synthetic methodology used to make them.

Synthesis

The nature of the C-C bond forming reaction to synthesize PPE based polymers was initially developed by Deick and Heck [36], Cassar [37], and Sonogashira et al. [38]. The general reaction involves the cross coupling of either an aryl bromide or iodide with a terminal alkyne (Figure 1.2), under palladium mediated conditions.

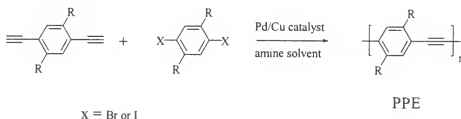


Figure 1.2: General reaction scheme for PPE formation.

The general mechanism [39] for this reaction is not entirely clear, but will give some insight with respect to its implications in PPE synthesis. It is generally accepted that substitution occurs through the initial formation of a bis(triphenylphosphine) dialkynylpalladium^{II} complex (**B**), which gives the active catalytic species bis(triphenylphosphine)palladium⁰ (**C**), through reductive elimination of a 1,3-butadiyne. Subsequent oxidative addition of an aryl halide to (**C**), followed

by an alkynylation of the adduct (**D**), gives an aryl-derivative of palladium (**E**). The latter regenerates the original bis(triphenylphosphine) palladium⁰ (**C**) through the reductive elimination of the desired coupling products. The alkynylation of the starting catalyst (**A**), or an oxidative adduct (**D**) in the catalytic cycle is

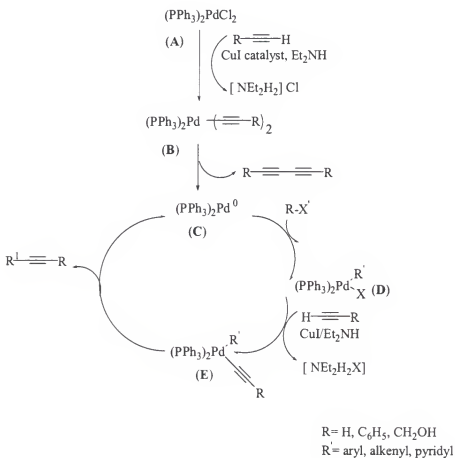


Figure 1.3: Proposed mechanism for the palladium mediated coupling of a terminal acetylene with an aryl halide [39].

catalyzed by cuprous iodide in the presence of an amine based solvent, typically triethylamine. Several of the critical factors that effect the polymerization, and in turn the molecular weight of the resulting polymer, are the choice of the aryl

halide, substituent choice on the haloarene, the type and amount of starting catalyst as well as the choice of solvents.

Early Attempts at PPE Synthesis

Some of the first attempts to make high molecular weight PPE polymers ultimately led to the formation of poorly soluble low-molecular weight polymers [39]. One such example of this involves the cross coupling of 1,4-didecyloxy-2,5-dibromobenzene (**G**) with 2,5-diethynyl-1,4-didecyloxybenzene (**F**) under conditions of PdCl_2 and $\text{Cu}(\text{OAc})_2$ to form the proposed PPE polymer [40] (Figure 1.4). The initially formed polymer was deep red in color, indicating a high degree of crosslinking, also clearly evident in the ^1H NMR is the presence of end group signals. This clearly contradicts Moroni's claim that the DP (degree of polymerization) was approximately 150. Based on the ^{13}C NMR and ^1H NMR spectra it is expected that these polymers have a DP of no more than 20. The cross-linking may be responsible for the GPC and light-scattering data and the massive overestimation of their molecular weights.

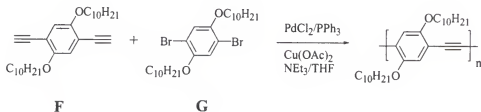


Figure 1.4: Scheme depicting Moroni's early attempt at high-molecular weight PPE synthesis [40].

An attempt to synthesize a much larger PPE based polymer was performed by Pu and coworkers, where an optically active binaphthyl monomer is coupled

with dibromo and diiodo benzene monomers (Figure 1.5). One example involves the coupling of 2,2'-bis(octadecyloxy)-6,6'-diethynyl-1,1'-binaphthyl (**H**) with 1,4-diiodobenzene under $\text{Pd(PPh}_3)_4$ / CuI conditions [41]. This polymerization was considered a success due to the lack of endgroups in the $^{13}\text{CNMR}$ and $^1\text{HNMR}$ spectra as well as the viscous nature of the resulting polymers. From light scattering and GPC measurements, it was estimated that the DP was roughly 75. Another significant point is that the resulting polymer was yellow in color, indicating that no significant cross-linking had taken place.

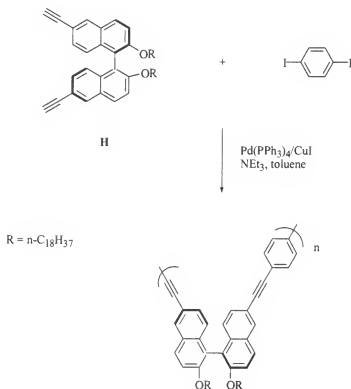


Figure 1.5: Pu's early work at synthesizing a high molecular weight optically active binaphthyl PPE polymer [41].

For the most part, neither of the above described works produced ultra high molecular weight PPE polymers, although their initial work contributed significantly to the understanding of the appropriate conditions needed to produce high-molecular weight PPEs. A detailed look at the individual conditions that effect this polymerization as well as the reaction mechanism might prove useful.

Haloaromatics (Iodide vs. Bromide)

The only two haloaromatics that are capable for use in high molecular weight PPE synthesis are the bromo and iodo derivatives. Although both have been shown to produce PPE polymers, substantial differences exist in their reactivity. Reaction of arylbromides typically require high reaction temperatures, while the corresponding aryliodides are known to react at or slightly above room temperature. It is proposed that the oxidative addition of **C** is more rapid for the aryliodides than for the bromides. The relative ease of oxidative addition of the aryl iodide to **C** is a function of the lower bond dissociation energy of the aryl iodide compared to the arylbromide. The advantage of using the aryl iodide is that the lower temperature used in the polymerization typically helps to prevent cross-linking of the PPE polymers and other structural defects that are prone to happen at higher temperatures.

Haloarene Substituent Effects

In comparing the reactivity of an electron rich and electron poor haloarene, one needs only to examine the active species (**C**) that it adds to. The palladium⁰ complex is electron rich (i.e., nucleophilic) and the oxidative addition of the haloarene should be influenced by the electronic properties of the

haloarene. This is clearly evident in that the more electron withdrawing the haloarene is, the faster its addition to the electron rich palladium⁰ complex. The more electron donating the haloarene is, the slower the oxidative addition is, and hence, the polymerizations proceeds much more sluggishly, and typically yields much lower molecular weight polymers.

Catalyst

One of the most influencing factors on these polymerizations is the choice of the appropriate palladium catalyst. For many years, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ was the catalyst of choice over $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}_2(\text{dba})_3$ (dba = 1,5-diphenyl-1,4-pentadien-3-one), largely because of the air stability of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ relative to the other palladium⁰ catalysts. It was noted that the formation of high molecular weight polymers was difficult using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ due to the observation by Swager that a small percentage of butadiyne defects were incorporated in the polymer due to this catalyst. In order to circumvent this problem, a small excess of terminal alkyne was necessary to produce high molecular weight polymers. The difficulty was in determining the exact excess that was needed, because a large excess of one monomer ultimately leads to low molecular weight polymers. Heitz, Moore, Wrighton, and Swager independently developed methods to eliminate this problem. All four groups came to the general consensus that a palladium⁰ catalyst was needed to avoid the dimerization to form butadiynes, as well as a 1-3 % excess of the terminal alkyne. The slight excess of terminal alkyne was necessary in that even with the Pd^0 catalyst, a small amount of unavoidable dimerization occurs. The difficulty with using $\text{Pd}(\text{PPh}_3)_4$ relates to

the air sensitive nature of this material. Extreme caution must be taken to eliminate even trace amounts of oxygen to produce high molecular weight polymers.

Solvents

The choice of solvent is critical to the formation of high molecular weight polymers. For the polymerization to be a success, two conditions must be met for the solvents. One, the amine base must be readily able to deprotonate the terminal alkyne at elevated temperatures, allowing for addition of the alkyne to the Pd^0 catalyst. Second, the co-solvent must be able to keep the growing PPE polymer in solution. The solvents of choice for these two conditions are diisopropylamine and triethylamine as well as THF and toluene for the solubilizing solvents. Although it is not clear why $(i\text{-Pr})_2\text{NH}$ and NEt_3 work so well in PPE synthesis, the choice of THF and toluene is readily apparent, owing to the excellent solvating ability of these two solvents for the growing polymer. Other bases such as piperidine, pyrrolidine, and morpholine have been used with success in small molecule synthesis but have had little success in large molecule (PPE) polymer synthesis.

High-Molecular Weight PPE Synthesis

Combining these conditions, one of the first true high-molecular weight PPE polymers was prepared by Swager and coworkers. The author's goal was to synthesize a PPE based polymer with a cyclophane unit appended to the backbone. The reaction of bisamide (**I**) with the diethynyl cyclophane moiety (**J**) yielded a PPE based polymer with an M_n of 300,000, corresponding to a

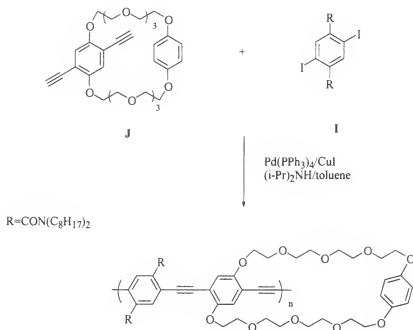


Figure 1.6: Cyclophane receptor based PPE polymer synthesized by Swager and coworkers [1].

DP > 300 (Figure 1.6) [1]. The high intrinsic viscosity of these polymers, as well as light scattering results, support the high-molecular weight assessments given to these polymers. The success of this polymerization centered on several key factors. First, the biamide (**I**) accelerated the coupling reaction due to its electron withdrawing nature, and second, a slight excess of the acetylene (**J**) was used to account for any oxidative dimerization to form butadiynes. Third, the co-solvents chosen were able to solvate the growing polymer, which is necessary to form high-molecular weight PPEs. And last, the active catalyst, $\text{Pd(PPh}_3)_4$, was chosen due to its propensity not to form butadiyne adducts. These cyclophane based PPE polymers showed significant fluorescence quenching when exposed to electron

acceptors such as paraquat (N,N' -dimethyl-4,4'-bipyridinium), leading to their possible application in chemical sensing based devices.

A more recent synthetic accomplishment by Swager was the synthesis of a new class of pentiptycene PPE based polymers with very high-molecular weights [33].

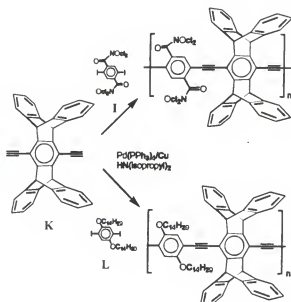


Figure 1.7: Scheme depicting the synthesis of a pentiptycene based PPE polymer synthesized by Swager and coworkers [33].

Swager's approach involved the coupling of diiodo-bisamide (**I**) and diiodo-dialkoxybenzene (**L**) with the bulky diethynylpentiptycene (**K**) under $\text{Pd(PPh}_3)_4/\text{CuI}$ conditions yielding two PPE polymers with a $\text{DP} > 500$ (Figure 1.7). The high-molecular weight of this polymer resulted from the appropriate choice of the diiodo-bisamide, for this monomer is activated by the presence of the diiodides as well as the electron acceptor characteristics of the bisamides. The author also claims that the bulky pentiptycene group increases the

solubility of the growing polymer, leading to the ultra high-molecular weight. This polymer is the highest molecular weight PPE polymer obtained by Pd-catalyzed coupling known to date. The interesting aspect of this pentapycticene PPE polymer is that it shows remarkable fluorescence sensitivity to nitroaromatic compounds, most notably 1,3,5-trinitrotoluene (TNT). This sensitivity to nitroaromatics has led to its direct application for sensing of explosives used in land mines.

With the rapid advances in synthetic methodology used in PPE synthesis, the device oriented applications of these materials have skyrocketed. A great deal of interest revolves around relating the structural properties of these polymers to their unique optical properties. In this regard, it is important to reliably define the molecular structure before proceeding to develop structure-property relations. As Wegner and Mullen point out [42, page 435] “there seems to be an uncertainty principle in the science of electronic materials according to which the interest aroused by structures increases with how poorly they are defined”. Precise models of conjugated polymers provide specific information concerning the solution, electronic, optical, thermal, and morphological properties of their higher homologs. Oligomers also serve as models for interpreting structural and conformational properties of a polymer. One key question to answer is, when does an oligomer begin responding like a polymer for a specific function? By building a series of oligomers and determining their optical properties (λ_{max} and band gap) or nonlinear optical response trends, one might be able to assess the degree of required polymerization to attain such a desired optical response from a polymer.

As the field of PPE synthesis has expanded in the last few years, the methodology used to create these polymers has been applied to synthesize oligomers. One of the pioneers in this field is J.M. Tour, who successfully developed an iterative approach to synthesize a series of oligo (phenylene-ethynylene)s (Figure 1.8). This iterative approach led to the creation of a series of oligomers ranging from dimers to a 16-mer, which is 128 Å in length [16]. The synthetic approach used to create these oligomers revolves around the TMS protected diethyltriazene (**DT**), which either can be cleaved under basic conditions to form the diethyltriazene protected terminal alkyne or reacted with iodomethane to form the TMS protected iodo derivative. Further step growth iterations utilizing these two compounds produced the desired oligomers in reasonable yield. The presence of the polar diethyltriazene functionality allowed for purification on silica gel.

A comparison of the absorption spectra of the oligomers to a typical PPE conjugated polymer reveals several interesting features. First, the bandgap of the oligomers is defined relatively early in the series, with a substantial red-shift occurring between the dimer and the octamer and little change thereafter. Most importantly though, the absorption maximum, $\lambda_{\text{max}} = 376$, is significantly bluer for these oligomers compared to a typical dialkoxy substituted PPE polymer, $\lambda_{\text{max}} = 450$ nm. This observation provided valuable information regarding the different electronic effects associated with alkyl and dialkoxy substitution. The electron rich nature of the dialkoxy substituted polymer donates electron density to the

polymer backbone and red-shifts the absorption spectrum. With the alkyl groups being a much poorer electron donor, the band-gap is blue-shifted by 75 nm.

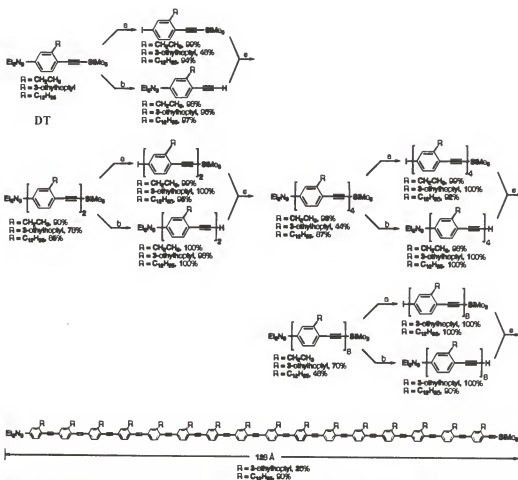
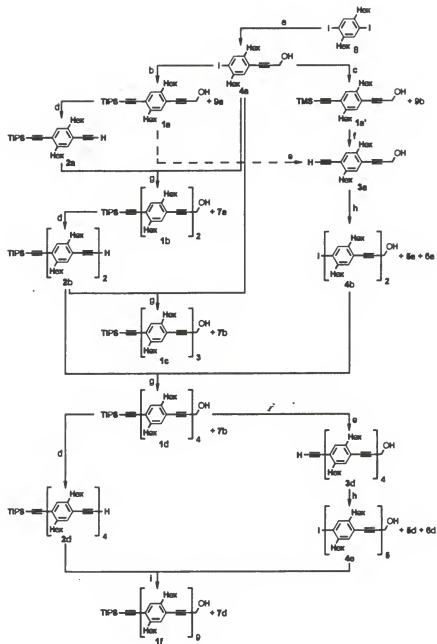


Figure 1.8: Iterative divergent/convergent synthesis of oligo(phenyleneethynylene)s [16].

Researchers in Godt's laboratory independently developed a similar approach based on the usage of a propargyl alcohol and triisopropylsilyl (TIPS)



Scheme 2. Key: (a) $\text{HC}\equiv\text{CCH}_2\text{OH}$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , piperidine, THF, room temp.; (b) $\text{TIPSC}\equiv\text{CH}$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , piperidine, THF, room temp.; (c) MnO_2 , KOH , diethyl ether, room temp.; (d) TBSCl , Et_3N , THF, room temp.; (e) NaOH , methanol, THF, room temp.; (f) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , piperidine, THF, room temp.; (g) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , piperidine, THF, room temp. or 8, $\text{Pd}_2(\text{dba})_3$, CuI , PPh_3 , piperidine, THF, room temp.; (h) 8, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , piperidine, THF, room temp. or 8, $\text{Pd}_2(\text{dba})_3$, CuI , PPh_3 , piperidine, THF, room temp.; (i) $\text{Pd}_2(\text{dba})_3$, CuI , PPh_3 , piperidine, THF, room temp., yields: see Table 1

Figure 1.9: Synthetic methodology used by Godt to create a series of oligo(phenyleneethynylene)s [43].

protecting groups [43]. The synthetic methodology allowed for the formation of a series of oligomers ranging from dimers to nonamers (Figure 1.9). Although the group was unable to carry out the iterations to the extent that Tour did, several valuable aspects arose from this work. First, the propargyl alcohol protecting group can be cleaved under much milder conditions (MnO_2 / KOH) than the diethyltriazene moiety in Tour's work, lessening the possibility of incorporating structural defects within the PPE backbone. Second, the diethyltriazene group is sufficiently more polar than the propargyl alcohol group, making silica gel chromatography on the prior much more difficult. Due to the structural similarities of Godt's polymers compared to those synthesized by Tour and coworkers, the absorption spectra showed near identical trends.

Metal-Organic π -Conjugated Polymers

The field of all organic π -conjugated polymers has been the focus of several major reviews over the past several years [44-46]. Although significant work has focused on all-organic polymers, relatively little work has been carried out concerning the photophysical properties of π -conjugated polymers that incorporate transition metal chromophores. This is surprising, given that the photophysics and excited state redox properties of many transition metal chromophores are tunable [47-49], and that this feature could be very useful in allowing one to tailor the photophysical properties of π -conjugated polymers.

Work by Yamamoto in the early 90's introduced a transition metal chromophore into a simple poly(arylene) structure [50]. A poly-2,2'-bipyridine (**Pbpy**) linear polymer was synthesized by dehalogenation polycondensation of

dihaloaromatic compounds and subsequently reacted with $\text{Ru}(\text{bpy})_2\text{Cl}_2$ to form the **Pbpy-Ru** complex (Figure 1.10). The absorption spectrum of the polymer was dominated by two transitions, a π, π^* absorption of the **Pbpy** backbone centered at 373 nm as well as an MLCT absorption at 450 nm. A strong emission band at 640 nm is observed for **Pbpy-Ru**, which is attributed to MLCT

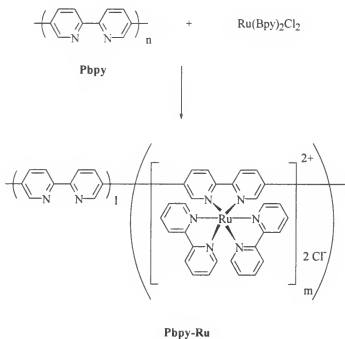


Figure 1.10: Poly(arylene) polymer synthesized by Yamamoto incorporating a $\text{Ru}(\text{bpy})_3^{2+}$ MLCT chromophore [50].

based emission. The electrochemical data were composed of the $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ oxidation as well as the reduction of the 2,2'-bipyridine unit. This suggests efficient electronic communication between the neighboring Ru centers and subsequently the **PBpy** backbone. The photophysics of Yamamoto's **Pbpy-Ru** polymer were largely neglected due to the polymer's insolubility, as well as the

fact that the author's objectives for studying these **Pbpy-Ru** polymers were aimed at examining their photocatalytic and photoelectrochemical properties.

Wright and coworkers synthesized an arylenethynylene polymer containing an η^6 $\text{Cr}(\text{CO})_3$ chromophore [51] (Figure 1.11). This polymer was a deep red solid, exhibiting very low solubility. It was noted that the $\text{Cr}(\text{CO})_3$ unit interacted with the extended π system, resulting in a red-shift for the chromium's charge transfer band. The focus of this work was oriented at examining the thermal stability of this complex, which along with the low solubility precluded any detailed photophysical studies.

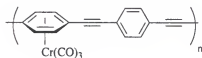


Figure 1.11: Structure of η^6 - $\text{Cr}(\text{CO})_3$ PPE polymer synthesized by Wright [51].

One significant work associated with the intercalation of a transition metal chromophore into a conjugated polymer was presented by Yu and coworkers [52]. This was the first work that introduced a $\text{Ru}(\text{bpy})_3^{2+}$ chromophore directly into the backbone of a PPV based polymer that produced a soluble polymer (Figure 1.12). The UV-vis spectra show some interesting features, with the all organic polymer ($x = 0$, $y = 1$ in Figure 1.12) exhibiting an intense π, π^* transition centered at 470 nm. The ruthenium doped polymers (polymers II - III) feature a similar band at 470 nm as well as a red-shifted band at 550 nm, which Yu attributed to the Ru

MLCT absorption. One important point is that the MLCT transition for these polymers is significantly red-shifted from that of $\text{Ru}(\text{bpy})_3^{2+}$, indicating strong

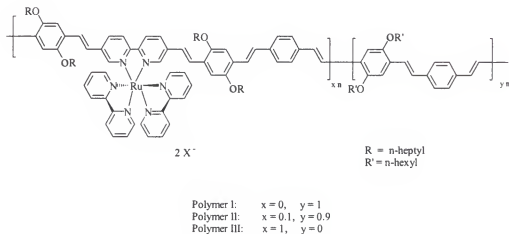


Figure 1.12: $\text{Ru}(\text{bpy})_3^{2+}$ containing PPV polymers synthesized by Yu and coworkers [52].

electronic communication between the Ru center and the organic PPV backbone. These polymers were shown to exhibit interesting photo-refractivity, photoconductivity and NLO responses. The drawback of this work was that little effort was made to thoroughly understand the complex photophysics of these systems.

An application of bpy-containing-PPV polymers in metal ion sensing was reported by Wasielewski and coworkers [53]. A new series of PPV based polymers that incorporated a 2,2'-bipyridine unit directly within the polymer backbone was synthesized (Figure 1.13). The choice of the 2,2'-bipyridine ring centered on its high binding constants to a variety of transition metal and main

group metal ions. When a metal ion coordinates to the 2,2'-bipyridine ring a conjugation enhancement is observed within the polymer backbone. This is due

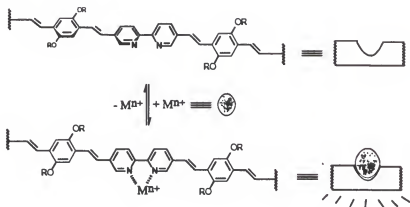


Figure 1.13: PPV metal ion sensing polymers synthesized by Wasielewski and coworkers [53].

to the fact that the unmetallated PPV polymer exhibits a conjugation break because of the lack of planarity of the 2,2'-bipyridine ring. When a metal ion coordinates to the bipyridine ring, the once non-planar bipyridine rings are forced planar due to the binding needs of the metal (Figure 1.14). This effect results in a conjugation enhancement within the polymer backbone, leading to different photophysical properties (red-shifted absorption and emission spectra) relative to the metal free polymer. These altered optical properties are due to the lowering of the polymer's band gap, which results from the conjugation enhancement and electrostatic effects induced by coordination of the metal. The most important point of this work was the degree of sensitivity that was achieved. For example,

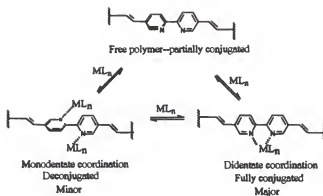


Figure 1.14: Effects of metallation on the PPV-bpy polymer [53].

when zinc(II), cadmium(II), mercury(II), palladium(II) and silver(I) were titrated into a solution containing the PPV – 2,2'-bipyridine polymer, the polymer π, π^* absorption band shifted from between 60 – 130 nm depending on the metal ion.

Objective of Present Study

The bulk of the work in the area of π -conjugated polymers and their transition metal doped counterparts has focused on device applications, rather than fundamental studies directed to gain a firm understanding of their photophysical properties. Much of the difficulty with examining the photophysical properties of these systems results from the difficulty in relating complex photophysical results to poorly defined structures or the poor solubility of the polymers. Recognizing the void in this area, we recently set out to synthesize and fully characterize the photophysics of a series of π -conjugated polymers and oligomers that contain transition metal chromophores as an integral component of the π -conjugated backbone. The structure of these polymers and

oligomers are based on the polyaryleneethynylene (PPE) architecture and they contain the *fac*-(bpy)Re^I(CO)₃Cl chromophore as an integral component of the π -conjugated backbone.

CHAPTER 2

PHOTOPHYSICS OF π -CONJUGATED POLYMERS THAT INCORPORATE METAL-TO-LIGAND CHARGE TRANSFER CHROMOPHORES.

Introduction

The central focus of this work is to investigate a series of poly(*p*-phenyleneethynylene) (PPE) based polymers that incorporate metal-to-ligand charge transfer (MLCT) chromophores as an integral component of the π -conjugated backbone. The structure of these polymers is based on the PPE architecture and they contain the *fac*-(bpy)Re^I(CO)₃Cl chromophore as an integral component of the π -conjugated backbone (Figure 2.1). Our hope is to combine the rich array of photophysics of the PPE polymers previously described with those of a transition metal chromophore.

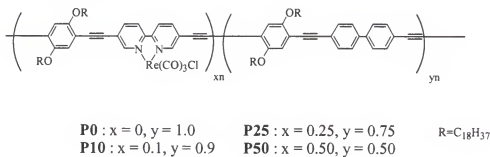


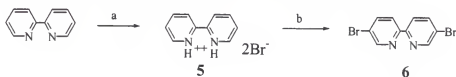
Figure 2.1: Structure of polymers **P0** - **P50**.

Unlike the PPE based polymers, Re^I chromophores tend to have quite different optical properties, which consist of a long lived low lying MLCT excited

state that is based on a $d\pi \rightarrow \pi^*$ (diimine) transition [49,54]. The MLCT state has been thoroughly studied in an array of $(\text{diimine})\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}$ complexes and is usually long-lived and luminesces in the red part of the visible spectrum [49,54,55]. Another valuable factor is that the MLCT excited state of typical Re^{I} chromophores tends to be a relatively strong oxidant, and therefore polymers with this chromophore may display unusual photoredox (or photoconductive) properties [49]. Unlike most of the prior metal polymer examples, which were either insoluble or soluble in only highly polar solvents such as water or DMF, the $(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}$ complex carries a neutral charge; consequently, the Re^{I} containing polymers are electrically neutral and soluble in low-dielectric solvents such as CHCl_3 and THF.

Synthesis

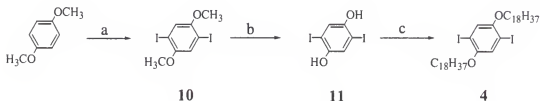
Figures 2.2 – 2.5 illustrate the structures and overall synthetic routes used to prepare the starting monomers, model compounds **1**, **5-L-1**, **5-Re-1** and polymers **P0** - **P50**. The key compound in these schemes is 5,5'-dibromo-2,2'-bipyridine (**6**) which is obtained by modification of a procedure developed by Ziessel and coworkers [56] (Figure 2.2). Further treatment of **6** with



a) acetyl bromide, MeOH; b) Br_2 , Δ , 4 days.

Figure 2.2: Modified procedure for the synthesis of 5,5'-dibromo-2,2'-bipyridine [56].

trimethylsilylacetylene in the presence of the $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ catalyst yielded 5,5'-diethynyl-2,2'-bipyridine (**8**) in high yield. The synthesis of 2,5-diiodo-1,4-dioctadecyloxybenzene (**4**) was effected by modification of a procedure reported by Swager and coworkers [33] (Figure 2.3).

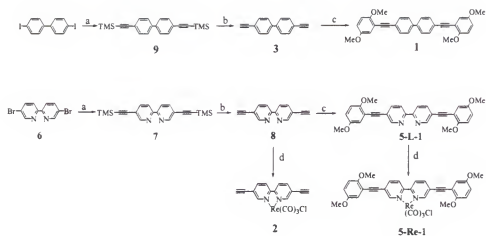


a) I_2 , KIO_3 , HOAc , H_2SO_4 ; b) BBr_3 , CH_2Cl_2 ; c) 1-bromooctadecane, DMF , KOH .

Figure 2.3: Modified procedure used for the synthesis of 2,5-diiodo-1,4-dioctadecyloxybenzene [33].

Once 5,5'-diethynyl-2,2'-bipyridine was available in good quantity, synthesis of the model compounds and polymers proceeded at a rapid pace. Thus, treatment of **8** with two equivalents of 2-iodo-1,4-dimethoxybenzene in the presence of $\text{Pd}(\text{PPh}_3)_4$ afforded dimethoxyphenylethynyl bipyridine (**5-L-1**) in good yield (Figure 2.4). Treatment of ligand **5-L-1** with one equivalent of $\text{Re}(\text{CO})_5\text{Cl}$ in refluxing toluene / CH_2Cl_2 produced model compound **5-Re-1**.

Polymers **P0** - **P50** were prepared via palladium mediated cross coupling as illustrated in Figure 2.5 [57,58]. The polymers differ with respect to the mole ratio of 4,4'-diethynylbiphenyl (**3**) and (5,5'-diethynyl-2,2'-bipyridine)- $\text{Re}^1(\text{CO})_3\text{Cl}$ (**2**) used in the polymerization reaction mixture. (In the acronym used to identify the polymers, Pn, the number indicates the mole % of **2**



a) Trimethylsilylacetylene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , THF, $(i\text{-Pr})_2\text{NH}$; b) KOH , MeOH , THF; c) 2-iodo-1,4-dimethoxybenzene, $\text{Pd}(\text{PPh}_3)_4$, CuI , THF, $(i\text{-Pr})_2\text{NH}$; d) $\text{Re}(\text{CO})_5\text{Cl}$, toluene, reflux

Figure 2.4: Synthesis of Model Compounds

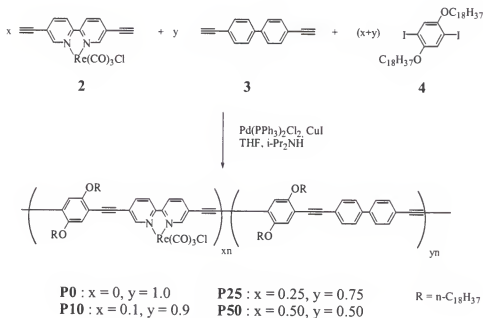


Figure 2.5: Scheme used to synthesize polymers **P0** - **P50**.

used in the reaction mixture. For example, in the synthesis of **P10**, the reaction mixture contains 90 mole % of **3** and 10 mole % of **2**.) Polymerization was effected under various reaction conditions using several different Pd catalysts including $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, $\text{Pd}(\text{dba})_2$ (dba = 1,5-diphenyl-1,4-pentadien-3-one) and $\text{Pd}(\text{PPh}_3)_4$. Optimal results were obtained with 5 mole % of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and 5 mole % of CuI in THF/diisopropylamine (2:1 v:v) at 70⁰ C for 16 hr.

Polymer Characterization

An important objective of the present investigation has been the structural characterization of metal and organic polymers **P0 - P50**. The structural characterization was effected on a series of polymers synthesized under identical conditions, the only variable being the mole fraction of the Re-containing diethynyl monomer (**2**) used in the reaction mixture. The resulting series of polymers **P0 - P50** were characterized by using gel permeation chromatography (GPC). The GPC method used to characterize **P0 - P50** relies on polystyrene standards to provide information regarding the molecular weight distribution of the polymer sample. Unfortunately, due to the significant structural differences between polymers **P0 - P50** and polystyrene (e.g., **P0 - P50** are rigid-rod polymers, while polystyrene is a random coil) molecular weight distributions determined by GPC do not provide information regarding absolute molecular weight of the polymers [59]. Despite this shortcoming, GPC data is useful in several ways. First, it provides a measure of the relative molecular weight distribution of a series of related polymers and, second, it allows one to determine the dispersion in the molecular weight distribution of a given polymer sample.

The dispersion is described by the polydispersity index (PDI) which is given by the ratio M_w / M_n , where M_w and M_n are, respectively, the weight- and number – average molecular weights of the sample [60].

GPC traces (Figure 2.6) and analysis are listed in Table 2.1. Several points are clear upon inspection of the GPC data. First, each polymer sample is characterized by a bimodal molecular weight distribution. The polymers are dominated by a single fraction (~95% chromatogram area) which has M_n ranging from 8-14 kD. However, each sample also exhibits a small high molecular weight fraction (~5% chromatogram area, $M_n > 100$ kD). This bimodal distribution is consistently observed, and apparently is characteristic of the methodology used to produce the “hairy rod” polyaryleneethynylene polymers. One possibility is that the high-MW fractions is due to cross-linked polymer chains that are formed by side reactions produced by the PdL_2 catalyst. A second possibility is that the high-MW fraction is a component of the sample that is physically cross-linked by entanglement of the octadecyl side chains. Table 2.1 contains listings of the M_w , M_n and PDI values determined for the polymer samples by using the entire chromatogram area and by using the area under the principal eluting fraction. The comparison clearly illustrates that the PDI and M_w values are skewed upwards significantly by the presence of the small, high molecular weight fraction. However, note that the M_n value, which better represents the composition of the bulk of the polymer sample (on a per mole basis), is not influenced significantly by the higher molecular weight fraction.

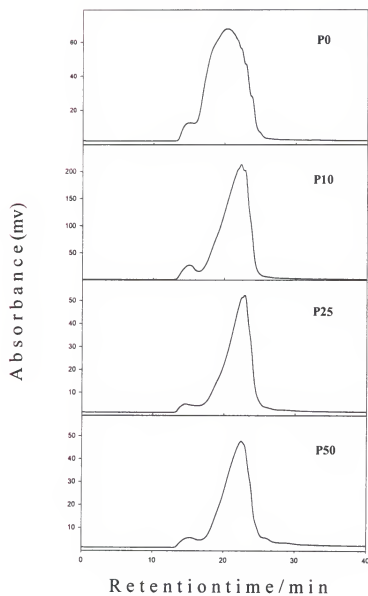


Figure 2.6: GPC traces of polymers **P0** – **P50** in THF solutions relative to polystyrene standards.

Table 2.1: GPC Analysis of Polymers **P0** – **P50**^a

Polymer	100 % of Chromatogram Area			95 % of Chromatogram Area	
	M_n / kD	M_w / kD	PDI	M_n / kD	M_w / kD
P0	15.2	79.7	5.2	13.5	37.4
P10	10.5	67.9	6.4	8.8	20.7
P25	8.9	69.2	7.7	7.9	16.4
P50	6.3	56.8	8.8	7.8	16.0

^a THF solutions, relative to polystyrene standards.

The next point that is evident from the GPC data is that the M_n values for the metal-organic polymers (e.g., **P10** – **P50**) are generally lower compared to that for the organic polymer **P0**. The lower M_n values for the metal-containing polymers likely reflects the fact that Re-bipyridine monomer **2** is less reactive in the Pd-catalyzed cross coupling reaction compared to the biphenyl monomer **3**. The impact that this difference in reactivity has on the structure of the polymer is unclear at present. However, if **2** is incorporated into the growing polymer chains more slowly than **3**, it is likely that the Re sites are dispersed within a polymer that is primarily organic, as opposed to being contained in segments dominated by Re-containing repeat units. While it is not possible to make any definitive

conclusions regarding the actual molecular weight of **P0 - P50**, comparison of the GPC data for the present polymers with that reported for structurally similar PPE-type rigid rod polymers implies that polymer samples **P0 - P50** likely consist of chains having 10 – 30 repeat units [59]. The carbonyl groups within the (bpy)Re^I(CO)₃Cl chromophore typically give rise to three clearly resolved IR bands in the 1900 – 2050 cm⁻¹ region [61]. FTIR analysis of the polymers **P10 - P50** in CCl₄ solution (Figure 2.7) confirms the presence of the intact Re(I) chromophore by the appearance of CO bands at 2024, 1930 and 1907cm⁻¹ (the a'(1), a'' and a'(2) bands, respectively). The approximate molar absorptivity for the a'(1) band in the (bpy)Re^I(CO)₃Cl chromophore was determined by examining the concentration dependence of the 2024cm⁻¹ FTIR absorption of (4,4'-(di-*tert*-butyl)-2,2'-bipyridine) Re^I(CO)₃Cl in CCl₄ ($\epsilon \sim 5000 \text{ M}^{-1}\text{cm}^{-1}$) (Figure 2.8). By using this value it is possible to estimate the concentration of the (bpy)Re^I(CO)₃Cl chromophore present in solutions of polymers **P10 - P50**. This information, in turn allows us to estimate the mole fraction of the (bpy)Re^I(CO)₃Cl repeat units (χ_{Re}) in the polymers. This analysis leads to values of $\chi_{\text{Re}} = 0.13, 0.26$ and 0.33 , respectively, for **P10**, **P25** and **P50**.

Photophysics of Model Compounds

The photophysics of model compounds **1**, **5-L-1** and **5-Re-1** were investigated to define the properties of the chromophoric units that comprise the metal-organic π -conjugated polymers. Table 2.2 contains a listing of many photophysical parameters for the compounds, including absorption maxima and

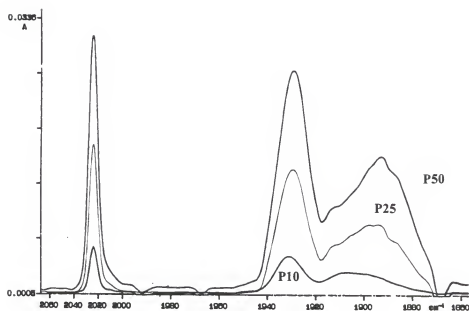


Figure 2.7: FTIR spectra of CO bands of polymers **P10** – **P50** in CCl_4 .

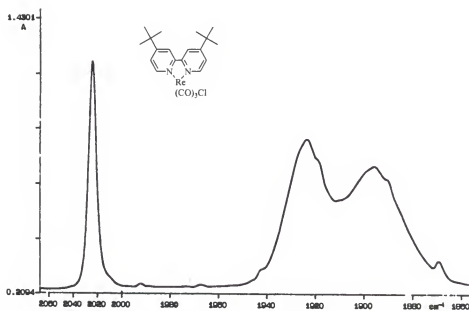


Figure 2.8: FTIR spectra of CO bands of $(4,4'-(\text{di-}t\text{-butyl})-2,2'\text{-bipyridine})\text{Re}(\text{CO})_3\text{Cl}$ in CCl_4 .

extinction coefficients, as well as emission maxima, quantum yields and lifetimes. Figure 2.9 compares the absorption and emission spectra of the three compounds at ambient temperature in THF solution and Figure 2.10 compares the emission spectra of **1** and **5-L-1** at 77K in a 2-methyl tetrahydrofuran (2-MTHF) solvent glass.

Organic compounds **1** and **5-L-1** display qualitatively similar absorption and fluorescence properties. The absorption of both chromophores is dominated by a comparatively intense near-UV transition which is due to the lowest π, π^* transition. In fluid solution, both compounds emit strong blue fluorescence ($\Phi_f \sim 1.0$) with a small Stokes shift, which is presumably due to the comparatively rigid structure of the compounds. The absorption and fluorescence maxima of the bipyridine **5-L-1** are red-shifted slightly relative to those for biphenyl **1**, apparently due to the effect of the bipyridyl nitrogens on the HOMO-LUMO gap. The fluorescence lifetimes of **1** and **5-L-1** are on the order of 1 ns, which is typical for π, π^* fluorescence [62]. The large fluorescence quantum yields coupled with the short lifetimes indicate that the radiative decay rates of both chromophores are very large ($k_r \sim 10^9 \text{ s}^{-1}$). The low temperature fluorescence spectra of **1** and **5-L-1** (Figure 2.10a) are unremarkable. The spectra are blue-shifted compared to the room temperature spectra and vibronic structure is observed. Phosphorescence was not detected in the low-temperature spectra of **1** and **5-L-1** for $\lambda < 800 \text{ nm}$. The absorption and luminescence properties of Re^{I} model complex **5-Re-1** differ significantly compared to those of the free bipyridine ligand **5-L-1**.

Table 2.2: Photophysical Properties of Model Compounds ^a

Compound	$\lambda_{\text{max abs}} / \text{nm}$ ($\epsilon_{\text{max}} / \text{M}^{-1} \text{cm}^{-1} \cdot 10^3$)	Assignment	$\lambda_{\text{max em}} / \text{nm}$ 298 K	Φ_{em} 298 K	$\tau_{\text{em}} / \text{ns}$ 298 K	$\lambda_{\text{max em}} / \text{nm}$ ^b 77K
1	314 (sh) (40.0) 352 (52.5)	π, π^* π, π^*	413	0.95	1.1	389
5-L-1	330 (40.5) 366 (56.5)	π, π^* π, π^*	470	0.95	2.4	413
5-Re-1	410 (29.0) 332 (34.0)	π, π^* IL & MLCT π, π^* IL & MLCT	433 (IL) 690 (MLCT)	< 0.001	< 1 ns (IL) 90 ns	410 590

^a Ambient temperature data for THF solutions and low-temperature data in 2-methyltetrahydrofuran (MTHF) glass. ^b 0-0 band in structured low- temperature spectrum.

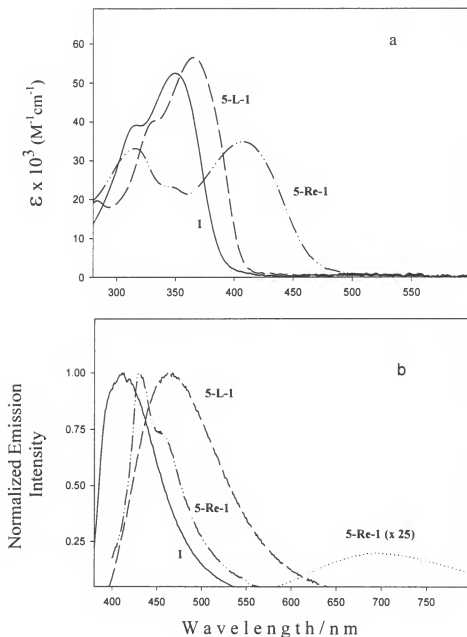


Figure 2.9: (a) UV-visible spectra of model compounds 1, 5-L-1, and 5-Re-1 in THF solution. (b) Luminescence spectra of model compounds 1, 5-L-1, and 5-Re-1 in THF at 298 K.

First, the absorption spectrum (Figure 2.9a) is dominated by a broad band with $\lambda_{\text{max}} = 410 \text{ nm}$. This band is red-shifted and has a significantly lower molar

absorptivity compared to the π, π^* absorption of the free ligand **5-L-1**. Complexes of the type (diimine) $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}$ typically feature a low-energy absorption ($\epsilon \sim 5.0 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) due to the $d\pi(\text{Re}) \rightarrow \pi^*$ (diimine) MLCT transition [47,54].

However, the molar absorptivity of the 410 nm band in **5-Re-1** is too large for an MLCT transition, and this implies that the low energy band is composed of mainly π, π^* intraligand (IL) character. This red-shift of the π, π^* transition in **5-Re-1** arises from a conjugation enhancement caused by the metal complex forcing the bipyridine rings from a non-planar cisoid conformation to a planar transoid conformation, increasing the conjugation length in the oligomer. It is likely that the MLCT transition is buried under the more intense π, π^* transition.

Figure 2.9b displays the room temperature emission spectrum of **5-Re-1** obtained with $\lambda_{\text{ex}} = 380 \text{ nm}$. First, it is important to note that although two emission bands are observed, the quantum yields of the emissions are very weak (Table 2.2). The emission spectrum is dominated by a relatively narrow band at $\lambda_{\text{max}} = 433 \text{ nm}$. The lifetime of the 433 nm emission is very short ($<1 \text{ ns}$), and on this basis we assign it to fluorescence from the $^1\pi, \pi^*$ IL state of the coordinated bipyridine ligand. The low quantum yield and the short lifetime of the π, π^* IL fluorescence arises because the IL state is quenched by fast intramolecular energy transfer to the MLCT manifold, which is at lower energy (vide infra). Fluorescence from π, π^* IL states is not typically observed in transition metal complexes: however, in **5-Re-1** the large radiative decay rate of the diphenyl ethynylbipyridine ligand allows fluorescence to “leak out” even though the π, π^* state is short lived. Interestingly, the π, π^* IL fluorescence is blue-shifted relative

to the position of the fluorescence of the free bipyridine ligand **5-L-1**. The blue-shift (and vibronic shoulder) in the π, π^* IL fluorescence is likely due to the fact that the chelated ligand is unable to relax along the inter-ring torsional mode after photoexcitation. In addition to π, π^* IL fluorescence, **5-Re-1** features a very weak, broad emission with $\lambda_{\text{max}} \sim 690$ nm and $\tau \sim 90$ ns. The characteristics of this emission strongly suggest that it can be assigned to the MLCT excited state.

Figure 2.10b illustrates two emission spectra of **5-Re-1** complex at 77K in MTHF, one collected with $\lambda_{\text{ex}} = 380$ nm and the second with $\lambda_{\text{ex}} = 450$ nm. The spectrum obtained with the shorter excitation wavelength shows two structured emission bands: one with $\lambda_{\text{max}} \sim 410$ nm and the second with $\lambda_{\text{max}} \sim 590$ nm. The spectrum obtained with the longer excitation wavelength features only the long wavelength emission. First, it is clear that the 410 nm emission band is due to fluorescence from the $^1\pi, \pi^*$ IL state of the diethynylbipyridine ligand. This assignment is supported by the fact that the position and the bandshape of this band is closely similar to that observed for free ligand **5-L-1** at 77 K (see Figure 2.10a). Assignment of the long-wavelength luminescence band is more dubious. A curious feature is that the bandshape of this emission is subtly different for 380 and 450 nm excitation. In particular, with 450 nm excitation the band features three clearly resolved vibronic transitions. By contrast, with 380 nm excitation, the resolution of the vibronic bands is poorer, and there is evidence for an underlying band on the 0,1 transition. Given this excitation wavelength dependence, we believe that the long-wavelength emission band is due to superposition of phosphorescence from the $^3\pi, \pi^*$ IL state and to luminescence

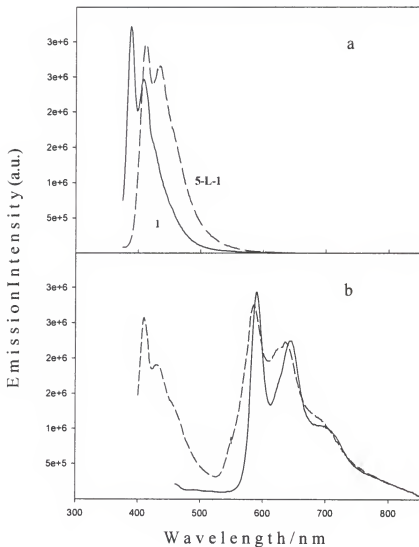


Figure 2:10: (a) Luminescence spectra at 77 K in 2-MTHF solvent glass.
 (a) Solid line, **1** ($\lambda_{\text{max}} = 350$ nm); dashed line, **5-L-1** ($\lambda_{\text{max}} = 350$ nm).
 (b) Dashed line, **5-Re-1** ($\lambda_{\text{max}} = 380$ nm); solid line, **5-Re-1** ($\lambda_{\text{max}} = 450$ nm).

from the $d\pi(\text{Re}) \rightarrow \pi^*$ MLCT state. Assuming that the MLCT state contributes to the long-wavelength emission, then the MLCT emission is blue-shifted approximately 2500 cm^{-1} compared to its position at 298 K (e.g., the band shifts

from 690 nm $\rightarrow$ 590 nm upon cooling). Such blue-shifts are characteristic for MLCT emission upon cooling to 77 K, and the 2500 cm⁻¹ shift observed for **5-Re-1** is typical [63,64].

Polymer Photophysics

The absorption spectra of **P0** – **P50** are compared in Figure 2.11a. The polymers feature an absorption band ($\lambda_{\text{max}} \sim 400$ nm) having an intensity that decreases with increasing χ_{Re} . This absorption band is similar in energy and bandwidth to the absorption of structurally-related PPE-type polymers [1,20,57,65], and on this basis it is assigned to the π, π^* transition of the conjugated polymer backbone. The Re-containing polymers **P10** – **P50** feature an additional absorption band ($\lambda = 440 - 540$ nm) with an intensity that increases with χ_{Re} . This long wavelength absorption is clearly associated with the incorporation of the (bpy)Re^I(CO)₃Cl chromophore into the polymer backbone, and is assigned to a π, π^* intraligand transition. This π, π^* transition mostly likely arises from an increased conjugation length within the polymer due to metal incorporation (similar to that observed for **5-Re-1**). Note that the π, π^* transition in the polymers is red-shifted significantly from the position in model complex **5-Re-1**. The red-shift likely arises because the π^*_{poly} orbital is significantly delocalized (and therefore stabilized) by the conjugated polymer backbone.

Excitation of solutions of **P0** – **P50** into the π, π^* absorption band produces a strong emission with $\lambda_{\text{max}} = 435$ nm and a shoulder on the long-wavelength side due to vibronic coupling (Figure 2.11b). The emission is Stokes-shifted only a small extent from the π, π^* absorption of the polymer backbone, and is assigned

to fluorescence from the $^1\pi,\pi^*$ exciton state. The $^1\pi,\pi^*$ assignment is supported by the fact that the fluorescence is very similar in energy and bandshape to that

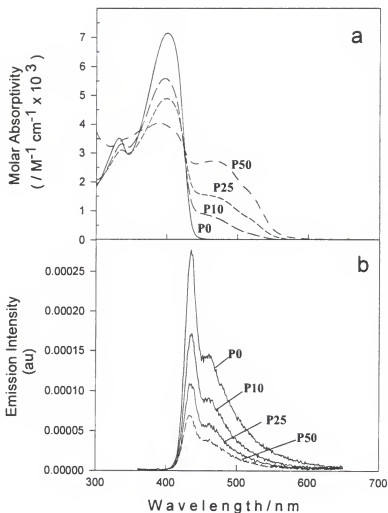


Figure 2.11: (a) Absorption spectra of **P0** – **P50** in THF solutions. Spectra were obtained on solutions having the same polymer concentration (mass per unit volume). Spectra are converted to a “molar absorptivity” scale dividing the concentration by the median molecular weight of the monomer repeat units. (b) Fluorescence spectra of **P0**– **P50** at 298 K ($\lambda_{ex} = 380$ nm). Spectra are normalized to reflect the quantum yields.

observed in related PPE- and PPV- type π -conjugated polymers [1,18,20,53, 65,67-69].

Fluorescence quantum yields (Φ_f) were determined for **P0 – P50** and the results are listed in Table 2.3. In general, Φ_f is comparatively large for all polymers; however, it is apparent that the Φ_f decreases as χ_{Re} increases. The fluorescence decay kinetics for solutions of **P0 – P50** (Table 2.3) are biexponential but are generally dominated by a large amplitude component with a lifetime of less than 1 ns. In order to facilitate comparison of the overall fluorescence decay kinetics of the different polymers, median lifetimes were computed according to the expression, $\langle\tau\rangle = \alpha_1\tau_1 + \alpha_2\tau_2$, where α_i and τ_i , are respectively, the normalized amplitude and lifetime of the i^{th} decay component recovered from the biexponential fits of the decays ($\langle\tau\rangle$, Table 2.3). Interestingly, the median fluorescence lifetimes for **P0 – P50** (like the fluorescence quantum yields) decrease as χ_{Re} increases. The parallel decrease in $\langle\tau\rangle$ and Φ_f with increasing χ_{Re} indicates that the $^1\pi,\pi^*$ exciton is quenched by the (bpy)Re^I(CO)₃Cl chromophore in the polymers. However, although quenching is observed, it is not particularly efficient at high χ_{Re} .

Further information regarding the excited state photophysics of **P0 – P50** comes from luminescence spectroscopy carried out at 77 K in MTHF solvent glasses. Figure 2.12 illustrates low temperature emission spectra of **P10 – P50** obtained with excitation into the π,π^* manifold of the π -conjugated polymer (λ_{ex} = 380 nm). First, at low temperature all of the polymer samples (including **P0**) exhibit fluorescence from the $^1\pi,\pi^*$ state of the polymer backbone. Remarkably,

Table 2.3: Photophysics of Polymers ^a

Polymer	λ_{max} abs / nm 298 K	Assignment	λ_{max} em / nm 298 K	Φ_{fl} 298 K	τ_1 / ns (α_1) 298 K	$\langle \tau \rangle$ / ns 298 K	λ_{max} em / nm 77 K
P0	400	π, π^*	435	0.28	0.81 (0.95) 6.39 (0.05)	1.1	443
P10	400 465 (sh)	π, π^* $\text{d}\pi \rightarrow \pi^*$ MLCT	435	0.16	0.72 (0.96) 2.19 (0.04)	0.78	443 643 ~ 690
P25	400 469 (sh)	π, π^* $\text{d}\pi \rightarrow \pi^*$ MLCT	435	0.11	0.32 (0.81) 1.04 (0.19)	0.48	443 643 ~ 690
P50	388 469	π, π^* $\text{d}\pi \rightarrow \pi^*$ MLCT	432	0.073	0.12 (0.46) 0.62 (0.54)	0.40	434 643 ~ 690

^a Ambient temperature data for THF solutions and low-temperature data in 2-methyltetrahydrofuran (MTHF) glass. ^b Quantum yield of the π, π^* fluorescence. ^c Lifetime (τ_1) and normalized amplitude (α_1) recovered from the fit of the π, π^* fluorescence decay to biexponential expression, $I(t) = \alpha_1 \exp\{-t / \tau_1\} + \alpha_2 \exp\{-t / \tau_2\}$. ^d Median lifetime calculated from the expression $\langle \tau \rangle = \alpha_1 \tau_1 + \alpha_2 \tau_2$.

the fluorescence band maximum and bandwidth is almost the same at room temperature in fluid solution and at low temperature in the glass. This

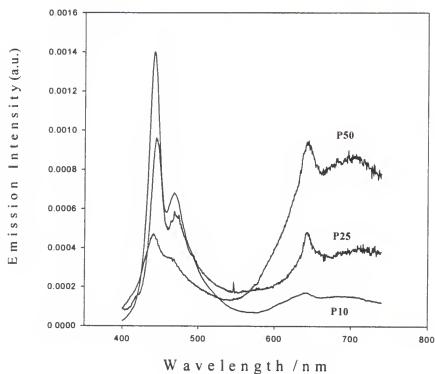
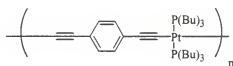


Figure 2.12: Luminescence spectra of polymers **P10** – **P50** in 2MTHF glass at 77 K ($\lambda_{\text{max}} = 380$ nm). Spectra were obtained on samples having equivalent concentration. Because of the sample and cryostat configuration it was difficult to maintain consistent sample position; therefore, relative emission intensities are only approximate. Small peaks in the 400 – 410 nm region are due to Raman scattering.

correspondence reveals very weak electron-phonon coupling in the fluorescent exciton state and implies that the exciton is very delocalized. At low temperature metal-organic polymers **P10** - **P50** exhibit additional emission band(s) in the red. This emission appears as a sharp band with $\lambda_{\text{max}} \sim 643$ nm (fwhm ~ 400 nm⁻¹) superimposed on a broad band with $\lambda_{\text{max}} \sim 690$ nm. We tentatively assign the

sharp 643 luminescence feature to phosphorescence from the $^3\pi,\pi^*$ state of the conjugated polymer backbone and the broad 690 emission to the $d\pi(\text{Re}) \rightarrow \pi^*_{\text{poly}}$ MLCT manifold. Although phosphorescence has previously not been observed in many π -conjugated polymer systems, our assignment is supported by the close similarity between the 643 nm luminescence and that observed from metal-organic PPE polymer **12** (Figure 2.13) [70].



12

Figure 2.13: Platinum - PPE polymer [70].

Thus, at 25 K **12** exhibits fluorescence at 405 nm (3.06 eV) and phosphorescence at 521 nm (2.38 eV, fwhm = 320 cm^{-1}); these spectral assignments indicate that in **12** the singlet-triplet (S-T) splitting is approximately 0.7 eV. Two points are significant when comparing the luminescence of **P10 - P50** and **12**. First, the width of the 0-0 phosphorescence band in **12** is 320 cm^{-1} , in good agreement with the width of the 643 nm feature in **P10 - P50**. Second, assuming that in **P10 - P50** the 443 nm (2.80 eV) emission is fluorescence and the 643 nm (1.93 eV) emission is phosphorescence, a 0.8 eV S-T splitting is computed, in close agreement with the S-T splitting for **12**.

At this point the MLCT assignment for the broad luminescence band underlying the $^3\pi,\pi^*$ phosphorescence is less solid. However, assuming that the MLCT assignment is correct, then the low temperature emission spectra imply

that the energy of the MLCT state in the polymers ($\lambda_{\text{max}} = 690 \text{ nm}$, 1.8 eV) is approximately 0.3 eV lower in energy than in model complex **5-Re-1** ($\lambda_{\text{max}} = 590 \text{ nm}$, 2.1 eV). This difference in the MLCT state energies derived from the low temperature emission spectra is at least consistent with the differences in the position of the MLCT absorption bands of **5-Re-1** ($\lambda_{\text{max}} = 406 \text{ nm}$, 3.05 eV) and the polymers ($\lambda_{\text{max}} = 460 \text{ nm}$, 2.70 eV).

Excited States in the Metal Containing Polymers

Based on the spectroscopic assignments for the absorption and luminescence data it is possible to construct a Jablonski diagram (Figure 2.14). In this diagram states arising from the organic component are at the left, while states arising from the metal-containing repeat units are at right. The state energies are

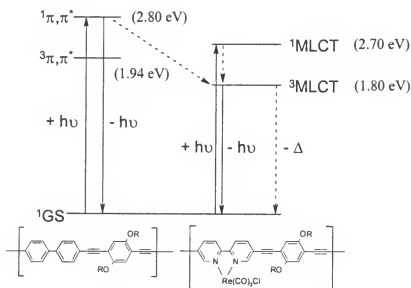


Figure 2.14: Jablonski diagram depicting the relative state energies determined via spectroscopic studies

based on the position of the luminescence band ($E_{\max}$) in the low temperature spectra, except for the $^1\text{MLCT}$ level which is based on the absorption band maximum. Thus, the $^1\pi,\pi^*$ and $^3\pi,\pi^*$ exciton states of the π -conjugated polymer backbone lie at 2.80 and 1.94 eV, respectively, while the $^1\text{MLCT}$ and $^3\text{MLCT}$ levels arising from the $d\pi \rightarrow \pi^*_{\text{poly}}$ transition lie at 2.7 and 1.8 eV, respectively. Excitation spectroscopy implies that energy transfer occurs from the $^1\pi,\pi^*$ exciton to the $d\pi \rightarrow \pi^*_{\text{poly}}$ $^3\text{MLCT}$ manifold, as anticipated based on the relative ordering of the states. On the other hand, the low temperature spectroscopy implies that the $^3\pi,\pi^*$ exciton and the $^3\text{MLCT}$ state are in close energetic proximity. Furthermore, the apparent observation of emission from both states at low temperature implies that the two states are either in equilibrium or are not rapidly interconverting. Recent studies of d^6 metal complexes indicate that a barrier to interconversion between $^3\pi,\pi^*$ IL and $^3\text{MLCT}$ states may exist when the two manifolds are in close energetic proximity [55,70,71]. A similar effect may be operating in metal containing polymers **P10 - P50**.

Discussion

In order for the Re^I sites to effectively quench the $^1\pi,\pi^*$ exciton, two processes must be rapid and efficient. First, the exciton must diffuse rapidly along the polymer backbone, effectively sampling an entire polymer chain during its lifetime (1ns). Second, the exciton must be trapped efficiently each time it comes within the encounter distance of a Re^I repeat unit. If both processes are rapid and efficient, quenching is expected to be efficient even at low χ_{Re} . Several studies imply that intrachain diffusion of a $^1\pi,\pi^*$ exciton (process 1 above) in π -

conjugated polymers is fast compared to its lifetime. For PPV-type polymer films, diffusion of "a relaxed exciton" (e.g., one that has migrated from a short to a long conjugation segment by ultrafast Forster transfer) is thermally activated, and the one-dimensional diffusion length of the relaxed exciton is approximated to be at 50 Å. Assuming that the data on the PPV films can be extrapolated to the PPE-type polymers in solution, a 50 Å diffusion length implies that, during its lifetime, a $^1\pi,\pi^*$ exciton will sample 10 or more repeat units. Another study supports the notion that in PPE type π -conjugated polymers the $^1\pi,\pi^*$ exciton samples a substantial fraction of a polymer chain during its 1 ns lifetime. Thus, Swager and co-workers demonstrated that an electron acceptor (paraquat) which is complexed to a cyclophane pendant group on a PPE-type polymer is extremely efficient at quenching an exciton [1]. This work, albeit qualitative, implies that during its lifetime the $^1\pi,\pi^*$ exciton has a diffusion length comparable to the length of a typical polymer chain (20 to 30 repeat units in Swager's study).

The other important process for exciton quenching is the trapping event (process 2 above). A significant body of data on small-molecule transition metal complexes implies that this process should also be rapid and efficient in the metal-organic π -conjugated polymers. Thus, the fluorescence of organic ligands coordinated to d^6 transition metals is strongly quenched in small-molecule complexes [72]. For example, this effect is clearly manifest in complex **5-Re-1**; free diimine ligand **5-L-1** is strongly fluorescent ($\Phi_f \sim 1$); however, only weak π,π^* IL fluorescence is observed from complex **5-Re-1**. The IL fluorescence is

quenched by intramolecular energy transfer to the MLCT manifold which is at lower energy compared to the IL state.

The experimental results on **P0 - P50** imply that at room temperature in fluid solution the Re^{I} sites are not particularly efficient traps for the $^1\pi, \pi^*$ exciton. However, the median fluorescence lifetime $\langle \tau \rangle$ decreases as χ_{Re} increases, which is consistent with a quenching mechanism that involves dynamic quenching of a diffusing exciton by the Re^{I} units. Unfortunately, the available data does not allow us to distinguish whether quenching is limited by exciton diffusion or exciton trapping by the metal complex sites. Given the large body of data on small molecule complexes which indicate that $^1\pi, \pi^*$ IL states are efficiently quenched by energy transfer to the MLCT manifold [72], we believe that the trapping event (process 2) should be very efficient in **P10 - P50**. Thus, we tentatively conclude that the relatively inefficient quenching in the metal-organic polymers is due to slow intrachain diffusion of the $^1\pi, \pi^*$ exciton.

Experimental

Photophysical Measurements

All sample solutions studied are either in THF or 2-MTHF (2-methyl-tetrahydrofuran) solutions. All photophysical studies were conducted in 1 cm quartz cuvettes. All room temperature studies were conducted on Argon bubble degassed solutions, and all low temperature studies were conducted on solvent glasses degassed by four freeze-pump-thaw cycles (ca. 10^{-4} Torr). For the absorption and emission studies, sample concentrations were adjusted to produce optically dilute solutions (i.e., $A < 0.20$ at all wavelengths).

UV-visible absorption spectra were collected on either an HP8452A diode-array or Varian Cary 100 dual-beam spectrometer. Corrected steady state emission measurements were conducted on a SPEX F-112 fluorimeter. Emission quantum yields were measured relative to 9,10-dicyanoanthracene ($\Phi_{em} = 0.89$) and perylene ($\Phi_{em} = 0.89$) in ethanol [66]. Time-resolved emission decays were observed with time-correlated single photon counting (FLT, Photochemical Research Associates; Excitation filter / source: Schott UG-11/H₂ spark (350 nm maximum) or 405 nm IBH NanoLED-07 laser diode; Emission filter 450 and 550 nm (**1**, **5-L-1** and **P0**) or 600 nm (**5-Re-1** and **P10 – P50**) interference filters). Lifetimes were determined by the observed decays with DECAN fluorescence lifetime deconvolution software [73]. Low temperature emission measurements were conducted in 1 cm glass tubes contained in an Oxford Instruments cryostat connected to an Omega CYC3200 automatic temperature controller.

General Synthetic

Diisopropylamine was distilled from KOH and tetrahydrofuran was distilled from sodium benzophenone ketyl and stored under argon. The synthesis of 2-iodo-1,4-dimethoxybenzene [74], and 2-iodo-1,4-dioctadecyloxybenzene [74] is described elsewhere. Copper(I) iodide, Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, 4,4'-diiodobiphenyl and 4,4'-bromobiphenyl were purchased from Aldrich Chemical Co. and used without further purification. Trimethylsilylacetylene was obtained from GFS chemicals and used without further purification. All cross-coupling reactions using Pd(PPh₃)₂Cl₂ and Pd(PPh₃)₄ were carried out under standard Schlenk and vacuum line techniques.

Monomer Synthesis

Protonated 2,2'-bipyridine (5)

35.5 mL of acetyl bromide (0.480 mol) was slowly added dropwise to 400 mL of methanol over a period of 1 hr. 15.0 g of 2,2'-bipyridine (0.096 mol) was then added and a yellow precipitate formed immediately, and the solution was allowed to stir for one additional hour. The solution was then carefully filtered and dried under vacuum, yielding 29.3 g of protonated 2,2'-bipyridine (5) (96%). $^1\text{H-NMR}$ (300 MHz, D_2O) δ 8.85 (d, 2H), 8.45 (s, 4H), 7.90 (m, 2H), 3.35 (s, 2H).

5,5'-Dibromo-2,2'-bipyridine (6)

Protonated bipyridine (5) (2.3 g, 0.0073 mol), and Br_2 (5 g, 0.0313 mol) were added to a glass reinforced tube and the tube was placed under vacuum for three consecutive free-pump-thaw cycles. The tube was then sealed and heated at 180°C for four days. The tube was allowed to cool and cooled with liquid nitrogen and carefully cracked behind a face shield with a hammer. The resulting orange solid was allowed to sit in the fume hood overnight, which allowed the excess bromine to evaporate. The resulting solid was dissolved in 125 mL of a 1 M NaOH solution to deprotonate the brominated bipyridine. The resulting aqueous solution was then extracted with 200 mL of chloroform three times, and the chloroform layers were combined. The solvents were then removed under vacuum, yielding a light tan solid. To the resulting tan solid was added 100 mL of acetone, and the solid that does not dissolve was collected by filtration. The white solid was then rinsed with excess acetone and allowed to dry, yielding pure

5,5'-dibromo-2,2'-bipyridine. The acetone rinse solutions were combined and the solvent removed under vacuum, these solids are a mixture of unreacted 2,2'-bipyridine and 5-bromo-2,2'-bipyridine. Overall, 1.10 g of 5,5'-dibromo-2,2'-bipyridine (48%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.70 (s, 2H), 8.28 (d, 2H), 7.95 (dd, 2H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 153.4, 150.0, 139.3, 122.0, 121.2.

5-Bromo-2,2'-bipyridine is isolated by dry packing on silica gel. The remaining solids (2,2'-bipyridine, 5-bromo-2,2'-bipyridine) were dissolved in 10 mL of chloroform and added to 10 g of silica gel. The chloroform was removed by roto-vap and the resulting powder was packed onto a preloaded column of silica gel (5 cm, packed in hexane) and the column was eluted with 100 mL of hexane. The solvent polarity was increased by adding diethyl ether (10% - 50%, 100 mL portions) and the first product off the column was 2,2'-bipyridine which eluted off as a long streaking band, 0.343 g. The band immediately following the 2,2'-bipyridine was the mono-bromo product, 5-bromo-2,2'-bipyridine, 0.326 g (19%). $^1\text{H-NMR}$ (300 MHz, CD_2Cl_2) δ 8.70 (d, 1H), 8.62 (d, 1H), 8.36 (d, 1H), 8.32 (d, 1H), 7.92 (dd, 1H), 7.79 (td, 1H), 7.30 (ddd, 1H). $^{13}\text{C-NMR}$ (75.4 MHz, CD_2Cl_2) δ 156.1, 151.1, 150.2, 140.4, 137.9, 125.0, 123.2, 122.1, 121.7.

5,5'-Trimethylsilyl ethynyl-2,2'-bipyridine (7)

5,5'-Dibromo-2,2'-bipyridine (6) (1.0 g, .0032 mol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.134 g, 0.191 mmol) and CuI (0.72 g, 0.380 mmol) were placed in a Schlenk flask and degassed. A degassed solution of THF (30 mL) and $(i\text{-Pr})_2\text{NH}$ (15 mL) was added along with trimethylsilylacetylene (2.25 mL, 0.016 mol). The solution was heated at 80°C for 12 hr, with heavy ammonium iodide salts forming

immediately. The solution was cooled, the solvents removed under vacuum, and the crude brown residue dissolved in diethyl ether. The solution was then passed through a short column of silica gel (3 cm) to remove the insoluble palladium catalyst. The solvents were removed and the crude tan solid was chromatographed on silica gel with a 80/20 chloroform/hexane solution, $R_f = 0.35$, yielding 1.05 (94%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.71 (s, 2H), 8.36 (d, 2H), 7.86 (dd, 2H), 0.26 (s, 18H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 154.5, 152.3, 140.0, 120.6, 119.5, 102.3, 99.5.

5,5'-Diethynyl-2,2'-bipyridine (8)

5,5'-Trimethylsilylethynyl-2,2'-bipyridine (**7**) (1.0 g, 0.0028 mol) was dissolved in 20 mL of THF and then 10 mL of MeOH was added. To this solution was added 5 mL of a 2 M NaOH solution, and the solution gelled immediately. The solution was stirred at room temperature for 6 hr. To this solution was added 20 mL of water along with 200 mL of chloroform. The chloroform layer was removed, dried over sodium sulfate and the solvents removed under vacuum. The crude tan solid was then chromatographed on silica gel with a 70/30 chloroform/hexane solution, $R_f = 0.25$, yielding 0.510 g of pure 5,5'-diethynyl-2,2'-bipyridine (89%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.76 (d, 2H), 8.39 (d, 2H), 7.89 (dd, 2H), 3.15 (s, 2H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 154.6, 152.3, 140.0, 120.6, 119.5, 81.6, 80.6.

5,5'-Diethynyl-2,2'-bipyridine $\text{Re}(\text{CO})_5\text{Cl}$ (**2**)

5,5'-Diethynyl-2,2'-bipyridine (**8**) (0.300 g, 0.0014 mol) and $\text{Re}(\text{CO})_5\text{Cl}$ [75] (0.580 g, 0.0016 mol) was dissolved in 20 mL of toluene and heated at reflux

for 30 minutes. At this time the solution was allowed to cool and the brick red precipitate was collected on a medium frit and rinsed with excess diethyl ether to remove excess starting material. The brick red solid was allowed to dry under vacuum overnight, yielding 0.678 g of **2** (95%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 9.10 (s, 2H), 8.10 (s, 4H), 3.55 (s, 2H). HRMS (FAB, positive ion, NBA) calcd for $\text{C}_{17}\text{H}_8\text{O}_3\text{N}_2\text{ReCl}$ (M^+) 509.977, found 509.977. Elem. Analysis: calcd for $\text{C}_{17}\text{H}_8\text{O}_3\text{N}_2\text{ReCl}$: C, 40.04; H, 1.58; N, 5.49; found: C, 39.74; H, 1.34; N, 5.22.

4,4'-Trimethylsilylethynylbiphenyl (9)

4,4'-Diiodobiphenyl (5.0 g, 0.0122 moles), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.258 g, 0.368 mmoles) and CuI (0.140 g, 0.737 mmol) were combined in a Schlenk flask and degassed with argon for 30 minutes. A degassed solution of THF (100 mL) and $(i\text{-Pr})_2\text{NH}$ (50 mL) was added along with trimethylsilylacetylene (7.90 mL, 0.056 mol), and a heavy precipitate formed immediately. The solution was heated under argon at 80°C for 16 hr, cooled and the solvents removed under reduced pressure. The resulting tan solid was dissolved in diethyl ether and passed through a plug (3 cm) of silica gel. The off white solid was then recrystallized from ethanol to yield a white solid, 3.47 g (82%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.53 (s, 8H), 0.27 (s, 18H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) 140.2, 132.4, 126.7, 122.4, 104.8, 95.2, -0.03.

4,4'-Diethynylbiphenyl (3)

4,4'-Trimethylsilylethynylbiphenyl (**9**) (1.0 g, 0.0028 mol) was dissolved in 20 mL of THF and 10 mL of MeOH was then added. To this solution was added 5 mL of a 2 M NaOH solution, and the solution gelled immediately. The

solution was stirred at room temperature for 6 hr. To this solution was added 20 mL of water along with 200 mL of chloroform. The chloroform layer was extracted, dried over sodium sulfate and the solvents removed under vacuum. The crude tan solid was recrystallized twice from ethanol yielding compound **3** as a white solid (91%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.55 (s, 8H), 3.15 (s, 2H).

2,5-Diiodo-1,4-dimethoxybenzene (10)

In a 1 L round bottom flask was added 300 mL of acetic acid, 3 mL of concentrated sulfuric acid and 30 mL of water. To this solution was added 1,4-dimethoxybenzene (5.0 g, 0.036 mol), I_2 (41.4 g, 0.163 mmol) and KIO_3 (15.5 g, .073 mol) and the resulting solution was stirred at reflux for 24 hr. The solution was allowed to cool and 300 mL of a 20% aqueous $\text{Na}_2\text{S}_2\text{O}_4$ was added to neutralize the iodine. At this time a yellow/tan solid fell out of solution. This solid was collected by vacuum filtration and dissolved in 200 mL of chloroform. A 200 mL solution of 2 M NaOH was added to quench the excess acid and the resulting chloroform layer was dried over sodium sulfate and the solvent removed under reduced pressure. The resulting white solid was allowed to dry, yielding 11.8 g of 2,5-diiodo-1,4-dimethoxybenzene (84%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.18 (s, 2H), 3.88 (s, 6H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 153.1, 121.4, 85.3, 57.0.

1,4-Diiodo-2,5-hydroquinone (11)

2,5-Diiodo-1,4-dimethoxybenzene (**10**) (10.0 g, 0.025 mol) was dissolved in 150 mL of dichloromethane and cooled to -80°C in an acetone/ CO_2 bath. To this stirred solution was slowly added a neat solution of BBr_3 (10 mL, 0.10 mol)

and after the addition the solution was allowed to warm up to room temperature. The solution was stirred for 12 hr at which time 100 mL of water was added to quench the excess BBr_3 , a precipitate formed immediately. To the resulting precipitate and aqueous/dichloro- methane solution was added 200 mL of a 2 M NaOH solution, at which time the aqueous layer turned dark black. The aqueous layer was poured off and cooled in an ice bath. A concentrated solution of HCl was then added dropwise (100 mL), and once the NaOH was neutralized, a brown precipitate began to form. Once the solution was significantly acidic, $\text{pH} \sim 1$, the brown solid was filtered and allowed to dry under vacuum overnight, yielding 8.56 g of 1,4-diiodo-2,5-hydroquinone (93%). $^1\text{H-NMR}$ (300 MHz, acetone) δ 8.98 (s, 2H), 7.27 (s, 2H). $^{13}\text{C-NMR}$ (75.4 MHz, acetone) δ 151.5, 124.6, 84.4.

2,5-Diiodo-1,4-dioctadecyloxybenzene (4)

1,4-Diiodo-2,5-hydroquinone (**11**) (5.0 g, 0.0138 mol), 1-bromo-octadecane (10.6 g, 0.0317 mol) was placed in a 100 mL round bottom flask. To the solids was added 60 mL of DMF and NaOH (10.0 g, 0.250 mol) and the solution was heated at reflux for 2 hr. The resulting solution was cooled and the solid filtered. The filtered solid was then rinsed with excess water and dissolved in 100 mL of chloroform and again extracted with water, 3x 200 mL. The resulting chloroform layer was dried over sodium sulfate and the solvents removed under reduced pressure. The crude brown solid was recrystallized from EtOH/chloroform twice to yield a white solid, 10.4 g (87%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.16 (s, 2H), 3.96 (t, 4H), 1.88 (m, 4H), 1.58 (m, 4H), 1.23 (br s, 56H),

0.88 (t, 6H). ^{13}C -NMR (75.4 MHz, CDCl_3) δ 152.6, 122.5, 86.0, 70.1, 31.7, 29.4, 25.8 (multiple), 22.5, 13.9.

Model Compound Synthesis

4,4'-Bis-[(2,5-dimethoxyphenyl)ethynyl]biphenyl (1)

4,4'-Diethynylbiphenyl (**3**) (0.300 g, 1.48 mmol), 2-iodo-1,4-dimethoxybenzene [**52**] (0.820 g, 3.10 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.063 g, 0.088 mmol) and CuI (0.034 g, 0.178 mmol) were placed in a 200 mL Schlenk flask that was purged with Argon. Tetrahydrofuran and diisopropylamine (8 mL and 5 mL, respectively) were added and the solution was heated at 70°C for 10 hr. Upon cooling, the reaction mixture was filtered to remove the insoluble Pd-byproducts and the solvents removed in vacuo. The crude product was dissolved in dichloromethane and passed through a short (3 cm) plug of silica gel, yielding a orange solid upon evaporation of the solvent. This material was purified by repeated recrystallization from toluene, yielding a light yellow solid, 0.420 g (67%). ^1H -NMR (300 MHz, CDCl_3) δ 7.63 (d, 8H), 7.08 (d, 2H), 6.86 (m, 4H), 3.89 (s, 3H), 3.79 (s, 3H). ^{13}C -NMR (75.4 MHz, CDCl_3) δ 154.5, 153.2, 139.9, 132.1, 126.7, 122.7, 118.0, 115.8, 112.9, 112.2, 93.2, 86.7, 56.5, 55.8. APCI MS calcd for $\text{C}_{32}\text{H}_{27}\text{O}_4$ [$\text{M}+\text{H}^+$]: 475; found 475.

5,5'-Bis[(2,5-dimethoxyphenyl)ethynyl]-2,2'-bipyridine (5-L-1)

2-Iodo-1,4-dimethoxybenzene (0.562 g, 2.16 mmol), 5,5'-diethynyl-2,2'-bipyridine (**8**) (0.200 g, 0.980 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.041 g, 0.058 mmol) and CuI (0.023 g, 0.120 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (8 mL) and diisopropylamine

(5 mL) was added to the Schlenk flask and the resulting solution was heated at 80⁰ C for 10 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with a 80:20 CHCl₃/hexane mixture afforded **5-L-1** as a pale-yellow solid, yield 358 mg (78%). TLC R_f = 0.25 (silica, 80:20 CHCl₃/hexane). ¹H NMR (CDCl₃) δ 8.83 (s, 2H), 8.42 (d, 2H), 7.96 (dd, 2H), 7.05 (d, 2H), 6.85 (m, 4H), 3.90 (s, 3H), 3.80 (s, 3H). ¹³C NMR (CDCl₃) δ 154.5, 153.9, 153.2, 151.6, 139.3, 120.7, 120.5, 117.9, 116.5, 112.1, 111.9, 90.3, 90.1, 56.4, 55.8. APCI MS calcd for C₃₀H₂₅N₂O₄ [M+H⁺]: 477; found 477.

fac-(5,5'-Bis[(2,5-dimethoxyphenyl)ethynyl]-2,2'-bipyridine)Re(CO)₃Cl (**5-Re-1**)

Compound **5-L-1** (0.100 g, 0.210 mmol) and Re(CO)₅Cl [75] (0.091 g, 0.252 mmol) were dissolved in 30 mL of toluene and the resulting solution was heated at 90⁰ C for 2 hr. The solution color changed from light yellow to orange. During the course of the reaction the blue fluorescence characteristic of **5-L-1** disappeared. The solution was cooled and the toluene was removed under vacuum, yielding the product as an orange solid. The complex was purified by repeated rinsing with toluene and diethyl ether. The pure metallated oligomer was obtained as an orange solid, yield 149 mg (90%). ¹H NMR (CDCl₃) δ 9.16 (s, 2H), 8.10 (br s, 4H), 7.07 (s, 2H), 6.96 (d, 2H), 6.89 (d, 2H), 3.91 (s, 6H), 3.82 (s, 6H). ¹³C NMR (CDCl₃) δ 196.7 (CO), 189.0 (CO), 155.3, 155.2, 153.2, 153.0, 140.5, 124.7, 122.6, 118.6, 117.9, 112.0, 110.8, 94.9, 87.5, 56.4, 55.9. HRMS (FAB, positive ion, NBA) calcd for C₃₃H₂₄O₇N₂ReCl (M⁺) 782.083, found 782.084; calcd for C₃₃H₂₄O₇N₂Re (M-Cl⁺) 747.114, found 747.112.

Synthesis of New Polymers

Polymer P0

4,4'-Diethynylbiphenyl (**3**) (44 mg, 0.220 mmol), 2,5-diiodo-1,4-dioctadecyloxybenzene (**4**) (190 mg, 0.219 mmol), Pd(PPh₃)₂Cl₂ (7.6 mg, 0.011 mmol) and CuI (2 mg, 0.011 mmol) were combined in 6 mL of diisopropylamine and 14 mL of tetrahydrofuran under nitrogen. The mixture was heated at 70°C for 16 hr. Through the course of the polymerization the solution became noticeably more viscous and highly fluorescent (blue). The reaction mixture was cooled to room temperature and then precipitated in acetone. The yellow precipitate was collected and washed repeatedly with hot acetone, hot acetonitrile, hot ethanol and hexane. Some lower molecular weight material was removed by the washings as evidenced by the fact that the washings were strongly fluorescent. After drying overnight at 40°C, 130 mg of **P0** was isolated as a yellow solid (73%). GPC (CHCl₃, polystyrene standards) $M_n = 13.5$, $M_w = 37.4$ kD (PDI = 2.7). ¹H-NMR (300 MHz, CDCl₃) δ 7.62 (br, s), 7.0 (br, s), 6.92 (br, s), 4.04 (br, t), 1.84 (br, m), 1.56 (br, m), 1.24 (br, s), 0.87 (br, t). ¹³C-NMR (75.4 MHz, CDCl₃) δ 153.7, 140.0, 132.1, 126.8, 122.8, 116.9, 114.0, 94.8, 87.0, 69.7, 32.0, 29.7, 29.4, 26.1, 22.7, 14.1.

Polymer P10

4,4'-Diethynylbiphenyl (**3**) (40 mg, 0.199 mmol), Compound **2** (11 mg, 0.022 mmol), 2,5-diiodo-1,4-dioctadecyloxybenzene (**4**) (190 mg, 0.219 mmol), Pd(PPh₃)₂Cl₂ (7.6 mg, 0.011 mmol), and CuI (2 mg, 0.011 mmol) were combined in 6 mL of diisopropylamine and 14 mL of tetrahydrofuran under nitrogen. The

mixture was heated at 70⁰ C for 16 hr. Through the course of the polymerization the solution became noticeably more viscous and slightly fluorescent (blue). The reaction mixture was cooled to room temperature and then precipitated in acetone. The red-orange precipitate was collected and washed repeatedly with hot acetone, hot acetonitrile, hot ethanol and hexane. Some lower molecular weight material was removed by the washings as evidenced by the fact that the washings were strongly fluorescent. After drying overnight at 40⁰ C, 115 mg of **P10** was isolated as a red-orange solid (62%). GPC (CHCl₃, polystyrene standards) $M_n = 8.8$, $M_w = 20.7$ kD (PDI = 2.3). ¹H-NMR (300 MHz, CDCl₃) δ 9.18 (br, s), 8.08 (br, s), 7.62 (br, s), 7.0 (br, s), 6.92 (br, s), 4.04 (br, t), 1.84 (br, m), 1.56 (br, m), 1.24 (br, s), 0.87 (br, t). ¹³C-NMR (75.4 MHz, CDCl₃) δ 153.7, 140.0, 132.1, 126.8, 122.8, 116.9, 114.0, 94.8, 87.0, 69.7, 32.0, 29.7, 29.4, 26.1, 22.7, 14.1.

Polymer P25

4,4'-Diethynylbiphenyl (**3**) (33 mg, 0.166 mmol), Compound **2** (28 mg, 0.055 mmol), 2,5-diiodo-1,4-dioctadecyloxybenzene (**4**) (190 mg, 0.219 mmol), Pd(PPh₃)₂Cl₂ (7.6 mg, 0.011 mmol) and CuI (2 mg, 0.011 mmol) were combined in 6mL of diisopropylamine and 14 mL of tetrahydrofuran under nitrogen. The mixture was heated at 70⁰ C for 16 hr. Through the course of the polymerization the solution became noticeably more viscous and slightly fluorescent (blue). The reaction mixture was cooled to room temperature and then precipitated in acetone. The red-orange precipitate was collected and washed repeatedly with hot acetone, hot acetonitrile, hot ethanol and hexane. Some lower molecular weight material was removed by the washings as evidenced by the fact that the washings were

strongly fluorescent. After drying overnight at 40⁰ C, 114 mg of **P25** was isolated as a red-brown solid (59%). GPC (CHCl₃, polystyrene standards) $M_n = 7.9$, $M_w = 16.4$ kD (PDI = 2.1). ¹H-NMR (300 MHz, CDCl₃) δ 9.18 (br, s), 8.08 (br, s), 7.62 (br, s), 7.0 (br, s), 6.92 (br, s), 4.04 (br, t), 1.84 (br, m), 1.56 (br, m), 1.24 (br, s), 0.87 (br, t). ¹³C-NMR (75.4 MHz, CDCl₃) δ 153.7, 140.0, 132.1, 126.8, 122.8, 116.9, 114.0, 94.8, 87.0, 69.7, 32.0, 29.7, 29.4, 26.1, 22.7, 14.1.

Polymer **P50**

4,4'-Diethynylbiphenyl (**3**) (22 mg, 0.111 mmol), Compound **2** (56 mg, 0.111 mmol), 2,5-diiodo-1,4-dioctadecyloxybenzene (**4**) (190 mg, 0.219 mmol), Pd(PPh₃)₂Cl₂ (7.6 mg, 0.011 mmol) and CuI (2 mg, 0.011 mmol) were combined in 6mL of diisopropylamine and 14 mL of tetrahydrofuran under nitrogen. The mixture was heated at 70⁰ C for 16 hr. Through the course of the polymerization the solution became noticeably more viscous. The reaction mixture was cooled to room temperature and then precipitated in acetone. The brick-red precipitate was collected and washed repeatedly with hot acetone, hot acetonitrile, hot ethanol and hexane. Some lower molecular weight material was removed by the washings as evidenced by the fact that the washings were strongly fluorescent. After drying overnight at 40⁰ C, 138 mg of **P50** was isolated as a dark red solid (65%). GPC (CHCl₃, polystyrene standards) $M_n = 7.8$, $M_w = 16.0$ kD (PDI = 2.0). ¹H-NMR (300 MHz, CDCl₃) δ 9.18 (br, s), 8.08 (br, s), 7.62 (br, s), 7.0 (br, s), 6.92 (br, s), 4.04 (br, t), 1.84 (br, m), 1.56 (br, m), 1.24 (br, s), 0.87 (br, t). ¹³C-NMR (75.4 MHz, CDCl₃) δ 153.7, 140.0, 132.1, 126.8, 122.8, 116.9, 114.0, 94.8, 87.0, 69.7, 32.0, 29.7, 29.4, 26.1, 22.7, 14.1.

CHAPTER 3

SYNTHESIS AND OPTICAL CHARACTERIZATION OF A SERIES OF BIPHENYLENE π -CONJUGATED OLIGOMERS

Introduction

Although our initial polymer work proved interesting and informative, several key questions remained regarding the photophysical properties of the previously synthesized polymers. One key question to address is why is energy transfer in the rhenium containing polymers seemingly so inefficient. Previous photophysical studies led us to suggest that one of two processes was responsible. One, the $^1\pi, \pi^*$ exciton generated after photoexcitation lacked the mobility to sample an entire polymer chain during its short 1 ns lifetime. This inability to migrate the full length of the polymer chain, perhaps to a segment of the polymer containing a rhenium trap site, would result in fluorescence from the $^1\pi, \pi^*$ excited state of the polymer backbone. Another option is that during the polymerization block polymers were produced, with some of the polymers failing to have a metal-organic segment. This would also account for the fluorescence, owing to the fact that even if a very small fraction of the polymers failed to have a metal site, the high quantum efficiency of an all organic polymer would most likely dominate the fluorescence spectroscopy. In order to address this question, we embarked on the synthesis and optical characterization of a series of π -conjugated oligomers that mimic the repeat structure of the polymers that were previously

synthesized. In addition to these oligomers, a controlled polymerization was developed that allowed for complete control over the resulting molecular structure of the polymer (Figure 3.1).

One of the greatest drawbacks to the random polymerization employed in the earlier polymerizations was the lack of control over the molecular structure of the resulting polymer. The more complex a molecular structure becomes, the more difficult it is to clearly assign the optical properties that are associated

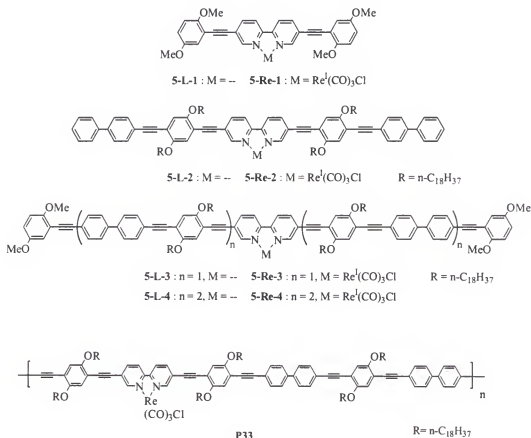


Figure 3.1: Structures of free oligomers, rhenium complexes and polymer P33.

with the molecule. By choosing to synthesize a series of oligomers we would have firm control over the resulting molecular structure, making it simpler to make clear assignments with regard to the photophysical properties of the oligomers. Another advantage to oligomer chemistry is associated with the ease of purification of oligomers relative to a large high molecular weight polymer. This is important because, even a small fraction of lower molecular weight material (perhaps polymer chains without a metal-organic segment) can skew the photoluminescent results. By synthesizing oligomers, one can purify them scrupulously through standard techniques such as column chromatography and repeated re-precipitation. This is significant in that it is well known that after the initial bond-forming reactions of a polymerization, as time proceeds the palladium catalyst is known to do additional insertion side reactions, thus altering the molecular structure of the polymer [42]. The advantage of oligomers is that they have a defined molecular structure that can be assigned via conventional techniques such as ^1H NMR, ^{13}C NMR and mass spectrometry.

Synthesis

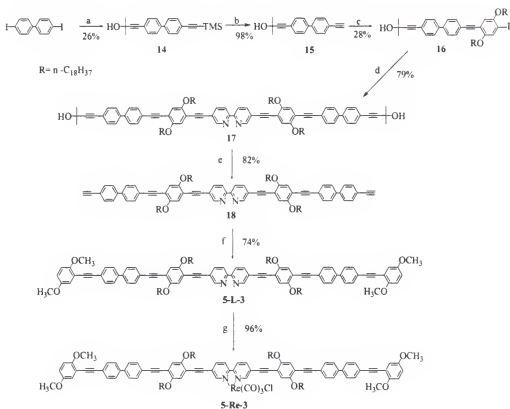
Clearly, the biggest challenge associated with the synthesis of a series of oligomers is choosing an appropriate synthetic methodology. Preparation of the series of free ligands and rhenium complexes 1-4 required an iterative strategy that uses Pd-mediated (Sonogashira) coupling chemistry to extend the PPE backbone outward from a 2,2'-bipyridine-5,5'-diyl "core". In order to implement this strategy a suitably functionalized "monomer" unit that contains a protected terminal acetylene or a protected (or masked) aryl iodide was required. Other

groups have previously reported application of the TMS group to protect terminal acetylenes and/or the 1-aryl-3,3-diethyl-triazene function as a masked aryl iodide in the synthesis of mono-disperse PPE oligomers [17,76,77]. The 1-aryl-3,3-diethyl-triazene masking group was deemed unsuitable for our needs owing to the possibility that the bipyridine nitrogens would react with the electrophile (MeI) that is used in the aryltriazene to aryl iodide conversion step. Although the TMS group seemed suitable for protecting the terminal acetylene, preliminary synthetic efforts aimed at preparing a monomer which contained an aryl iodide and a TMS-protected acetylene were thwarted due to the difficulty of separating the desired product from unreacted starting materials and by-products. This problem is easily visualized when considering the coupling reaction of 1,4-diiodobenzene with 1 equivalent of TMS-acetylene, which results in the formation of three products, unreacted 1,4-diiodobenzene, the desired product 1-iodo-4-trimethylsilyl-ethynylbenzene and the bis-substituted product, 1,4-bis-trimethylsilylethynylbenzene. The chromatographic separation is difficult (if not impossible) because the starting materials, the by-products and the desired product are all non-polar and therefore have similar solubility and comparative R_f values.

Monomer and Oligomer Synthesis

We finally discovered that the 2-methyl-3-buten-2-ol (2-MP) protecting group would allow us to readily prepare and purify multigram quantities of monomer **16** (Figure 3.2), which features a protected terminal acetylene and a reactive aryl iodide. Thus, in a two-step, one-pot procedure 4,4'-diiodobiphenyl was reacted with trimethylsilylacetylene (TMSA) and then with 2-methyl-3-buten-

2-ol to afford compound **14**. The 2-MP protecting group in **14** allows this compound to be separated from the reaction by-products by silica gel chromatography. The separation is facile because the by-products have

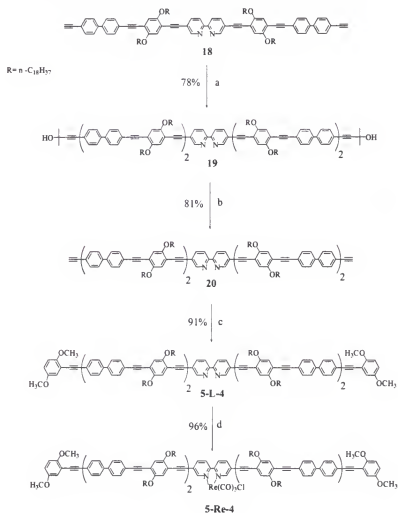


a) 1eq. TMSA(stepwise addition), xs 2-methyl-3-butyn-2-ol, Pd(PPh₃)₂Cl₂, CuI, THF, (i-Pr)₂NH; b) KOH, THF, MeOH; c) 1,4-diiodo-2,5-di(2-methoxyphenyl)benzene, Pd(PPh₃)₂Cl₂, CuI, THF, (i-Pr)₂NH; d) 5,5'-diethynyl-2,2'-bipyridine, Pd(PPh₃)₂Cl₂, CuI, THF, (i-Pr)₂NH; e) KOH, toluene, reflux; f) 2-iodo-1,4-dimethoxybenzene, Pd(PPh₃)₂Cl₂, CuI, THF, (i-Pr)₂NH; g) Re(CO)₅Cl, toluene.

Figure 3.2: Synthesis of Oligomer **5-L-3** and **5-Re-3**.

significantly higher or lower R_f values compared to compound **14** owing to the polar 2-MP protecting group. Selective removal of the TMS group from **14** with

KOH/MeOH afforded mono-protected compound **15**. Monomer **16** was obtained by coupling **15** with 1 equivalent of 1,4-diiodo-2,5-dioctadecyloxybenzene. Here again the polarity of the 2-MP protecting group in **16** allowed this material to be easily separated from the reaction by-products, affording the pure compound in

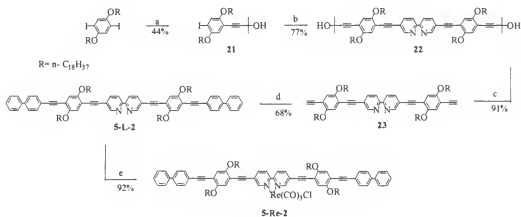


a) 2 eq. **16**, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, $(i\text{-Pr})_2\text{NH}$; b) KOH, toluene, reflux; c) 2-iodo-1,4-dimethoxybenzene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, $(i\text{-Pr})_2\text{NH}$; d) $\text{Re}(\text{CO})_5\text{Cl}$, toluene.

Figure 3.3: Synthesis of **5-L-4** and **5-Re-4**.

28% yield after chromatography. Once **16** was available in multigram quantities, synthesis of the desired oligomers proceeded rapidly. Thus, reaction of 2 equivalents of **16** with 5,5'-diethynyl-2,2'-bipyridine produces **17** which is subsequently deprotected by KOH, toluene and heat to afford **18**. Endcapping of **18** with 2-iodo-1,4-dimethoxybenzene affords **5-L-3**, and subsequent metallation of **5-L-3** with $\text{Re}(\text{CO})_5\text{Cl}$ in toluene yields **5-Re-3**. A further iterative sequence beginning with coupling of **18** with 2 equivalents of **16** followed by and endcapping affords oligomer **5-L-4** followed by metallation to afford **5-Re-4** (Figure 3.3).

As shown in Figure 3.4, oligomer **5-L-2** was synthesized by a different approach that also relies upon the 2-MP protecting group. First, 1,4-diiodo-2,5-dioctadecyloxy benzene was coupled with 1 equivalent of 2-methyl-3-butyn-2-ol



- a) 2-methyl-3-butyn-2-ol, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, (i-Pr)₂NH;
 b) 5,5'-diethynyl-2,2'-bipyridine, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, (i-Pr)₂NH;
 c) KOH, toluene, reflux; d) 4-bromobiphenyl, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, (i-Pr)₂NH; e) $\text{Re}(\text{CO})_5\text{Cl}$, toluene, reflux

Figure 3.4: Synthesis of **5-L-2** and **5-Re-2**.

to produce **21**. This compound was readily separated from unreacted starting material owing to the polar 2-MP function. Reaction of 2.0 equivalents of **21** with 5,5'-diethynyl-2,2'-bipyridine afforded **22**, which was deprotected to **23** by KOH, toluene and heat. Finally, **23** was coupled with 4-bromobiphenyl to produce **5-L-2** which is subsequently metallated to afford **5-Re-2**.

Polymer Synthesis

The synthesis of **P33** proved to be quite challenging. The key compound in the synthesis of **P33** is compound **29b** (see Figure 4.5). The reaction of **29b** with $\text{Re}(\text{CO})_5\text{Cl}$ yielded compound **35** in excellent yield (the synthesis and characterization of compounds **29b** and **35** is described in Chapter 4). Reaction of **16b** with rhenium compound **35** produced **P33** in reasonable yield (Figure 3.5).

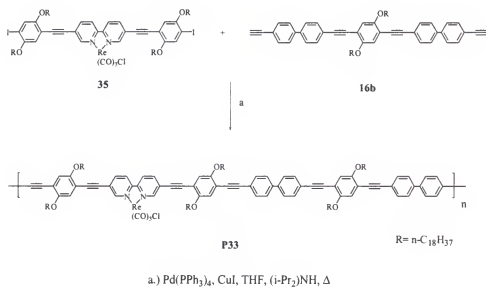


Figure 3.5: Scheme depicting the controlled synthesis of **P33**.

UV-Visible Absorption Spectra

Figure 3.6 compares the UV-visible absorption spectra of the free oligomers with those of the corresponding (L)Re(CO)₃Cl complexes, where L = oligomer. The free oligomers all feature two absorption bands in the 300 – 500 nm region. The lower energy transition of the oligomer corresponds to a long-axis polarized π, π^* transition while the higher energy band corresponds to a short-axis polarized π, π^* transition. Rhenium complexes, **5-Re-1** – **5-Re-4** exhibit similar bands in the UV-visible compared to the free ligand, with the noticeable difference that a significant red-shift is observed for the long-axis polarized transition along with a smaller red-shift for the short-axis polarized transition. Figure 3.7a compares the UV-visible spectrum of **P33** with **P50**, these spectra are nearly identical to the spectrum of **5-Re-4**. The extinction coefficients for the free oligomers and metal complexes are given in Tables 3.1 and 3.2, respectively.

Emission Spectroscopy

Oligomers **5-L-1** – **5-L-4** all exhibit strong fluorescence in the blue region of the spectra, as shown in Figure 3.8. This fluorescence is very similar to that observed for other PPE based polymers and also similar to our previously studied polymers [18,43]. The radiative decay rates are very high for these free oligomers, with each oligomer possessing a high quantum yield (Φ_{em}), listed in Table 3.2. The emission lifetimes for oligomers **5-L-1** – **5-L-4** are extremely short (~1 ns), again consistent with other phenylene-ethynylene based polymers [1], Table 3.2.

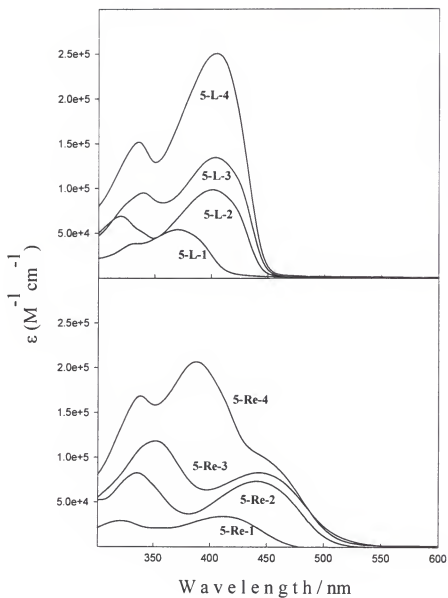


Figure 3.6: Absorption spectra of (a) 5-L-1 – 5-L-4 and (b) 5-Re-1 – 5-Re-4. Spectra are acquired on THF solutions at 298 K.

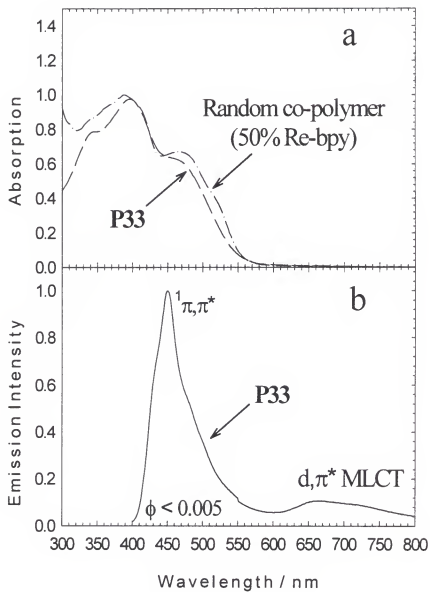


Figure 3.7: (a) Absorption spectra of **P33** and random polymer **P50**. (b) Emission spectrum of **P33**. Spectra are acquired on THF solutions at 298 K.

Table 3.1: Photophysical Properties of Biphenylene Oligomers.^a

Oligomer	λ_{max} abs / nm ($\epsilon_{\text{max}} / \text{M}^{-1}\text{cm}^{-1} \cdot 10^4$)	Assignment	$\lambda_{\text{max}}^{\text{b,c}}$ em / nm 298 K	$\Phi_{\text{em}}^{\text{d}}$ 298 K	$\tau_{\text{em}}^{\text{b,e}} / \text{ns}$ 298 K
5-L-1	330 (3.85)	π, π^*	470	0.89	2.4
	370 (5.40)	π, π^*			
5-L-2	320 (6.90)	π, π^*	454	0.72	0.95
	400 (9.80)	π, π^*			
5-L-3	340 (9.50)	π, π^*	454	0.68	1.1
	404 (13.5)	π, π^*			
5-L-4	336 (15.2)	π, π^*	453	0.79	0.68
	406 (25.1)	π, π^*			

^aTHF solutions at 298K. ^b Samples are argon degassed. ^cMaximum of fluorescence band. ^dFluorescence quantum yields measured by using actinometers as described in text. ^eFluorescence decay lifetimes.

Table 3.2: Photophysical Properties of Biphenylene Rhenium Complexes.^a

Complex	$\lambda_{\text{max}}^{\text{abs}} / \text{nm}$ ($\epsilon_{\text{max}} / \text{M}^{-1} \text{cm}^{-1} \cdot 10^4$)	Assignment	$\lambda_{\text{max}}^{\text{em}} / \text{nm}$ 298 K	$\tau_{\text{em}}^{\text{c}} / \text{ns}$ 298 K	$\tau_{\text{em}}^{\text{c}} / \mu\text{s}$ 80 K
5-Re-1	332 (2.90) 410 (3.40)	π, π^* π, π^*	586	14	6.24
5-Re-2	336 (8.30) 440 (7.34)	π, π^* π, π^*	659	154	2.49
5-Re-3	352 (11.8) 444 (8.30)	π, π^* π, π^*	643	174	5.11
5-Re-4	338 (16.8) 388 (20.7) 444 (10.3)	π, π^* π, π^* π, π^*	644	172	7.61

^aTHF solutions at 298K. ^bMaximum of MLCT band, samples are argon degassed. ^cEmission decay of MLCT excited state.

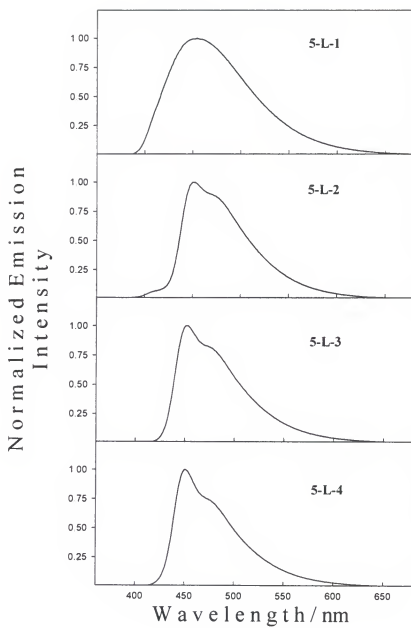


Figure 3.8: Emission spectra of oligomers **5-L-1** – **5-L-4** in argon degassed THF solutions at 298 K. Excitation wavelength is 350 nm.

The rhenium complexes exhibit a very weak fluorescence and due to its similarities to the free ligand, is attributed to trace impurities remaining from the metallation reaction. A very weak broad red-shifted emission is observed for the

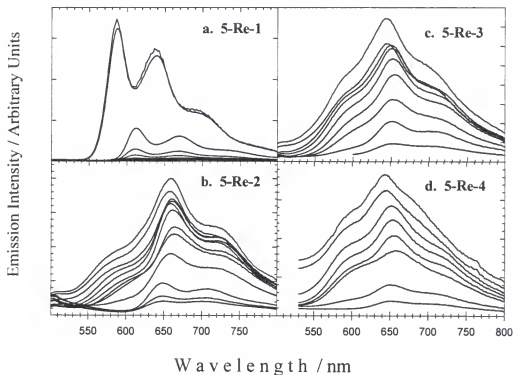


Figure 3.9: Emission spectra of the **5-Re** complexes in 2-MTHF (440 nm excitation) at various temperatures ranging from 298 K to 80 K. Emission intensity increases with decreasing temperature, and spectra are in 20 K increments. (a) **5-Re-1**; (b) **5-Re-2**; (c) **5-Re-3**; (d) **5-Re-4**

rhenium complexes. Luminescence spectra were recorded at varying temperatures ranging from 298K to 80K, as shown in Figure 3.9. Lifetimes for the low-energy emission at 298K and 80 K and emission maxima for the complexes are given in Table 3.2. A very weak fluorescence ($\Phi_f < 0.005$) is observed for

polymer **P33** (Figure 3.7b) and based on the similarities to the **5-Re** fluorescence is also assigned to impurities. The long-wavelength room temperature emission of **P33** appears very similar to that of the **5-Re** series, with a sharp emission band at 650 nm buried under a broad emission band extending out into the red portion of the spectrum.

Discussion

The key factor dominating the electronic absorption and emission spectra of the oligomers and rhenium complexes is the relative conjugation length of the oligomer. By placing biphenyl spacers within the backbone of the oligomer we introduce a conjugation break within the oligomer. It is well known that the ground state geometry of the biphenyl molecule has the two phenyl rings bent $\sim 43^\circ$ out of the plane [78] (Figure 3.10). This lack of planarity causes a significant

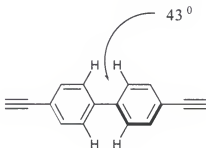


Figure 3.10: Ground state geometry of the biphenyl molecule.

conjugation break within the backbone of the oligomer. With this in mind, one would expect the effective conjugation length to increase as long as the oligomer backbone remained planar (i.e., no biphenyl spacers). An increase in conjugation length is defined as a lowering of the $^1\pi,\pi^*$ absorption energy of the oligomer.

Upon the incorporation of a biphenyl unit, one would expect to see a drop off in further conjugation enhancement. The largest conjugation enhancement is expected between the smaller oligomers **5-L-1** and **5-L-2** respectively, due to the fact that they are mostly planar, with only **5-L-2** having a biphenyl spacer on its peripheral. Also important to note is that there is approximately a 20° dihedral angle between the two pyridine planes in 2,2'-bipyridine when it is in its transoid-like conformation [79]. This lack of planarity of the pyridine rings also prevents the oligomer from being fully conjugated. As the size of the oligomer increases, along with the number of biphenyl spacers, little to no enhancement is expected in the conjugation length of the oligomer because the biphenyl unit causes significant disruption within the oligomer backbone, restricting the chromophore length to the central "planar" portion of the oligomer.

It is also anticipated that metallation of the oligomers would also increase the effective conjugation length. This is because incorporation of a metal ion forces the bipyridine rings from a transoid conformation to the necessary cisoid conformation needed for coordination to the metal center. This geometric change should help to increase the conjugation within the oligomer backbone. An increased conjugation length throughout the oligomer backbone should red-shift the π, π^* absorption of the complex. Similar trends were observed by Wasielewski and coworkers in their PPV-Bpy polymer, which experienced large red-shifts in the polymers absorption spectra when exposed to a series of metal ions (Figure 3.11) [53]. Taking this information into account, a detailed analysis of how the

conjugation length manifests itself in the oligomer's photophysics will be discussed.

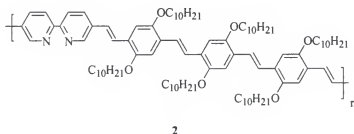
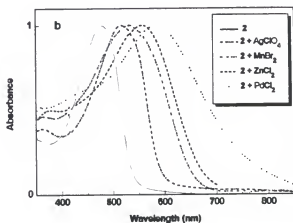


Figure 3.11: Absorption spectra in CHCl_3 at room temperature for metal complexes of polymer 2 [53].

UV-Visible Absorption Spectra

The conjugation length of oligomers 5-L-1 – 5-L-4 is defined very early in the series, which is clearly evident in the fact that a substantial red-shift in the π, π^* (HOMO $\rightarrow$ LUMO) transition occurs between oligomers 5-L-1 and 5-L-2 (370 nm $\rightarrow$ 400 nm). As the oligomers increase in size, no further lowering of the π, π^* energy is observed, owing to the lack of planarity of the biphenyl units

within the backbone of oligomer **5-L-3** and **5-L-4**. For example, throughout the series of oligomers the lowest energy transition corresponds to a $^1\pi,\pi^*$ absorption centered on the central segment of the oligomer (Figure 3.12) defined by the bipyridine core extending to the first biphenyl group. This again is supported by the fact that little change is observed in the energy

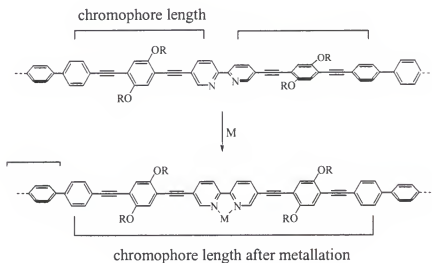


Figure 3.12: Diagram depicting the chromophore length prior to and after metallation.

of this transition between oligomers **5-L-3** and **5-L-4**, with each having the same backbone structure, minus one of the biphenyl repeat units. It is worth noting that as the molecular size of the oligomers increases, a noticeable enhancement in the oscillator strength of both π,π^* transitions is observed. This is reasonable in that as the size of the oligomer is increasing, the number of light harvesting chromophores in solution is increasing, accounting for the large increase in the extinction coefficients.

One of the most interesting aspects of this work involves the photophysical changes that the oligomer undergoes upon metallation with rhenium. Between **5-Re-1** and **5-Re-2** a substantial red-shift is observed for the lower energy π, π^* (HOMO $\rightarrow$ LUMO) transition, but this spectral feature remains relatively constant for **5-Re-3**, **5-Re-4** and **P33**. This red-shift of the π, π^* transition of the free oligomer in the metal complex is associated with the metal bonding in a bidentate fashion, forcing the bipyridine rings into a planar conformation (Figure 3.12). There is little change in the oscillator strength of this transition for the larger rhenium oligomers, leading us to conclude that this transition is largely composed of the central bis (phenylethynyl-dialkoxy-phenylethynyl)-capped bipyridine portion of the oligomer. This chromophore is likely confined by the twisting of the first biphenyl unit in the oligomer backbone, restricting any further delocalization into the peripheral segment of the oligomer. In general the larger oligomers, notably **5-Re-4**, seem to behave as a dual component system, one, an organic segment composed of the outer peripherals of the conjugated oligomer, followed by a metal-organic central segment, restricted by the twisting of the first biphenyl unit. It is important to note that the existence of $d\pi(\text{Re}) \rightarrow \pi^*$ oligomer MLCT transition is buried under the more intense π, π^* transition. This is evident in the fact that MLCT transition typical of rhenium complexes lies in the 400 - 450 nm region and has a very weak absorptivity ($\epsilon \sim 1000$ to $5000 \text{ M}^{-1}\text{cm}^{-1}$) [54].

Emission Spectroscopy

The emission spectra for the oligomers **5-L-1** – **5-L-4** are unremarkable. All oligomers exhibit an intense short lived emission in the blue region of the spectrum. Based upon the exceedingly short lifetime (~ 1 ns) of this emission it is assigned to fluorescence from the singlet excited state of the oligomer. The quantum efficiencies for the fluorescence are high, again typical of rigid-rod type molecules, which are unable to relax vibrationally after photoexcitation. The quantum yields (Φ_f) and fluorescence lifetimes for the series of oligomers decreases as the size of the oligomer increases. This may be due to aggregation between oligomers or the formation of the triplet state of the oligomer backbone.

Our primary interest lies in the emission properties of the rhenium complexes, **5-Re-1** through **5-Re-4**. It is well known that typical diimine complexes of the general formula (diimine)Re(CO)₃Cl do not exhibit fluorescence due to the non-radiative pathways introduced by the presence of the transition metal [49]. Our initial prediction was that we should see strong quenching of the ligand fluorescence accompanied by either MLCT based emission or triplet phosphorescence from the ligand backbone. We were initially disturbed to see a very weak fluorescence from the series of metal complexes, but careful comparison between the free ligand fluorescence and that of the rhenium complexes led us to believe that it was merely a trace impurity from the metallation process. The portion of the spectrum that was of primary interest was the long-wavelength emission observed for the rhenium complexes. It is well known that (diimine)Re(CO)₃Cl complexes exhibit red-shifted emission that is

attributed to emission from a $^3\text{MLCT}$ state [49,54,55]. At low temperature this emission is usually structured and relatively strong. All four of the rhenium oligomers exhibit weak emission at room temperature and a slightly structured emission at 80K. Based upon the lifetimes, this emission is assigned to luminescence from a $^3\text{MLCT}$ excited state. It is interesting to compare the low-temperature luminescence spectra of the four rhenium complexes. The smallest rhenium complex, **5-Re-1**, exhibits a very highly structured emission at low temperature, while the larger rhenium complexes (**5-Re-2** through **5-Re-4**) all have much less structured emission (Figure 3.9). This again is consistent with the overall increase in molecular complexity that is associated with the larger metal complexes. At low temperature **5-Re-1** has a very well defined emission, which is consistent with a smaller amount of distortion in the excited state. As the larger complexes begin to freeze, a significant amount of distortion can occur along the oligomer backbone, as each individual biphenyl can be locked into a series of conformations, each giving rise to a slightly different excited state. These various conformations lead to a distribution of "effective" conjugation lengths and consequently, different $^3\text{MLCT}$ energy levels. By slightly perturbing the energy levels, we see an overall broadening of the emission spectra, which increases as the complexity of the backbone increases. Another factor that can contribute to the broad band structure of the oligomers is the possibility that the emission has some $^3\pi,\pi^*$ character. This is not possible to rule out due to the fact that each of the emission decay traces seems to indicate a low amplitude long lived component (tens of μs). Electronic excitation and absorption measurements confirm that there

is excellent communication between the oligomer π, π^* and the $d\pi(\text{Re}) \rightarrow \pi^*$ MLCT excited states, since excitation into the former produces emission from the latter. The lifetimes of the rhenium complexes (~ 150 ns), is typical for that of a $^3\text{MLCT}$ excited state, along with a small decay component attributed to the triplet state of the oligomer. It is interesting to note that as the effective conjugation length increases the lifetimes increase, this is clearly evident in that the lifetime of **5-Re-1** is only 14 ns, while the lifetime of the largest rhenium complex, **5-Re-4**, is nearly 175 ns. This drastic increase in $^3\text{MLCT}$ lifetimes is consistent with an excited state that is more delocalized through the oligomer backbone. Although the trends are not completely consistent, it appears that as the effective conjugation length is increased, the lifetime of the $^3\text{MLCT}$ increases.

The lack of noticeable fluorescence from **P33** seems to indicate that we generated block polymers in the previously synthesized polymers **P0** – **P50**. Regrettably due to the lack of solubility of this polymer, detailed photophysical studies other than room temperature fluorescence and absorption studies were not possible.

Based upon spectroscopic results a Jablonski diagram can be constructed for the series of rhenium complexes, as shown in Figure 3.13. It is clear that photoexcitation can produce the $^3\text{MLCT}$ state either by production of the singlet π, π^* followed by internal conversion to the $^3\text{MLCT}$ state, or by direct population, as shown in the diagram.

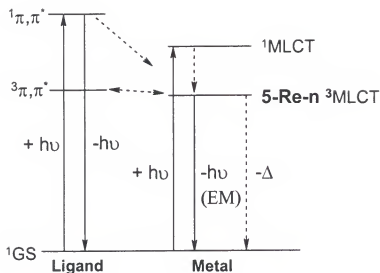


Figure 3.13: Jablonski diagram of **5-Re-n** excited state energy levels [80].

Conclusion

The primary objective of this work was oriented at addressing our initial concerns relating to the apparent inefficiency of energy transfer in the rhenium containing polymers. Through the rational design of oligomeric complexes with repeat units that mimic the structure of our original polymers, we were able to address this question. Our oligomeric studies were significant in that several key questions were answered. First, the low energy absorption in the UV-Visible spectrum for the rhenium containing polymers was not an MLCT absorption, instead this transition is a red-shifted π, π^* absorption induced by the conjugation enhancement induced by metallation. Second, due to the lack of any π, π^* fluorescence in the rhenium containing oligomers and **P33**, we are able to conclude that energy transfer in these π -conjugated systems is highly efficient,

removing our concern that the exciton generated upon photoexcitation lacked mobility. Taking this into account, our initial concern that we were producing block polymers seems to explain our puzzling photophysical results with regard to our earlier synthesized polymers. By increasing the % of metal loading in our previously synthesized polymers (P50 for example), the probability of having a polymer without a rhenium chromophore goes down, which in turn explains the decreased quantum yields, relative to the lower loading polymers (P10 for example).

Experimental

Photophysical Measurements

All sample solutions studied are either in THF or 2-MTHF (2-methyl-tetrahydrofuran) solutions. All photophysical studies were conducted in 1 cm quartz cuvettes. All room temperature studies were conducted on Argon bubble degassed solutions, and all low temperature studies were conducted on solvent glasses degassed by four freeze-pump-thaw cycles (ca. 10^{-4} Torr). For the absorption and emission studies, sample concentrations were adjusted to produce optically dilute solutions (i.e., $A < 0.20$ at all wavelengths).

Absorption spectra were collected on either an HP8452A diode-array or Varian Cary 100 dual-beam spectrometer. Corrected steady state emission measurements were conducted on a SPEX F-112 fluorimeter. Emission quantum yields were measured relative to 9,10-dicyanoanthracene ($\Phi_{em} = 0.89$) and perylene ($\Phi_{em} = 0.89$) in ethanol [40]. Time-resolved emission decays were

observed with time-correlated single photon counting (FLT, Photochemical Research Associates; Excitation filter/source: Schott UG-11/H₂ spark (350 nm maximum) or 405 nm IBH NanoLED-07 laser diode; Emission filter 450 and 550 nm (**5-L** oligomers) or 600 nm (**5-Re** complexes) interference filters). Lifetimes were determined by the observed decays with DECAN fluorescence lifetime deconvolution software [73]. Low temperature emission measurements were conducted in 1 cm glass tubes contained in an Oxford Instruments cryostat connected to an Omega CYC3200 automatic temperature controller.

General Synthetic

Diisopropylamine was distilled from KOH and tetrahydrofuran was distilled from sodium benzophenone ketyl and stored under argon. The synthesis of 2-iodo-1,4-dimethoxybenzene[74], and 2-iodo-1,4-dioctadecyloxybenzene [74] is described elsewhere. Copper(I) iodide, Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, 4,4'-diiodobiphenyl and 4,4'-bromobiphenyl were purchased from Aldrich Chemical Co. and used without further purification. Trimethylsilylacetylene, 2-methyl-3-butyn-2-ol was obtained from GFS chemicals and used without further purification. All cross-coupling reactions using Pd(PPh₃)₂Cl₂ and Pd(PPh₃)₄ were carried out under standard Schlenk and vacuum line techniques.

Synthesis

Compound 14

4,4'-Diiodobiphenyl (5.75 g, 14.2 mmol), Pd(PPh₃)₂Cl₂ (298 mg, 0.426 mmol) and CuI (162 mg, 0.852 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of trimethylsilylacetylene (2.0

mL, 14.2 mmol), tetrahydrofuran (45 mL) and diisopropylamine (30 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 3 hr. Heavy ammonium iodide salt formed immediately. After 3 hr 2-methyl-3-butyn-2-ol (7.0 mL, 71.0 mmol) was added. The solution turned from light yellow to dark black and heating was continued for an additional 6 hr. The solution was allowed to cool and after evaporation of the solvent the product was chromatographed on silica gel with 80:20 CHCl₃/hexane affording **14** as a white solid, yield 1.22 g (26%). The first product of the column (R_f = 1), is a mixture of di-silylated biphenyl and unreacted 4,4'-diiodobiphenyl, followed by compound **14** (R_f = 0.3) and finally the bis-substituted alcohol, (R_f = 0.1). ¹H NMR (CDCl₃) δ 7.51 (m, 8H), 2.18 (s, 1H), 1.64 (s, 6H), 0.27 (s, 9H). ¹³C NMR (CDCl₃) 140.1, 139.9, 132.4, 132.1, 126.7, 126.6, 122.3, 121.9, 104.8, 95.2, 94.6, 81.8, 31.4, -0.05. EI-MS calcd for C₂₂H₂₄OSi: 332; found 332.

Compound 15

Tetrahydrofuran (40 mL), methanol (20 mL) and a 20% aqueous NaOH solution (5 mL) were added to **14** (1.0 g, 3.0 mmol) and the resulting solution was stirred rapidly. The mixture, which immediately became viscous, was stirred at room temperature for 5 hr. The reaction mixture was diluted with 100 mL of water and extracted with CHCl₃ (3 x 100 mL). The organic layer was separated, dried and the solvent evaporated leaving a white solid, affording 730 mg of **15** (94%). TLC R_f = 0.3 (silica, CHCl₃/hexane, 80:20). ¹H NMR (CDCl₃) δ 7.54 (m, 8H), 3.15 (s, 1H), 2.18 (s, 1H), 1.64 (s, 6H). ¹³C NMR (CDCl₃) 140.5, 139.8, 132.6, 132.0, 126.7,

126.6, 122.1, 121.3, 94.7, 83.4, 81.8, 78.1, 65.6, 31.4. EI-MS calcd for $C_{19}H_{16}O$: 260; found 260.

Compound 16

Compound **15** (1.0 g, 3.84 mmol), 1,4-diiodo-2,5-dioctadecyloxybenzene (**6**) (3.33 g, 3.84 mmol), $Pd(PPh_3)_2Cl_2$ (0.08 g, 0.115 mmol) and CuI (0.044 g, 0.230 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of THF (50 mL) and diisopropylamine (50 mL) was added to the solids and the resulting solution was heated to 80° C and stirred for 3 hr. After evaporation of the solvents, the crude solid was purified by chromatography on silica gel with 70:30 $CHCl_3$ /hexane to afford 1.07 g of **16** (28%). The first product of the column ($R_f = 1$), is the non-polar unreacted 1,4-diiodo-2,5-dioctadecyloxybenzene (**6**), followed by compound **16** ($R_f = 0.4$). ^1H NMR ($CDCl_3$) δ 7.54 (m, 8H), 7.31 (s, 1H), 6.92 (s, 1H), 3.98 (m, 4H), 2.18 (s, 1H), 1.83 (br m, 4H), 1.64 (s, 6H), 1.51 (br m, 4H), 1.25 (br s, 56H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$) δ 154.3, 151.8, 140.0, 139.9, 132.1, 131.9, 126.8, 126.7, 123.8, 122.7, 121.9, 115.8, 113.5, 94.6, 93.9, 87.6, 86.6, 81.9, 70.1, 69.8, 65.6, 31.9, 31.4, 29.7, 29.3, 26.0, 22.7, 14.1. EI-MS calcd for $C_{61}H_{91}IO_3$: 999; found 999.

A major by-product of this reaction is the di-substituted product, 2,5-bis-[4'-(3-hydroxy-3-methyl-1-butynyl)biphenylethynyl]-1,4-dioctadecyloxybenzene. This material is recovered as a yellow solid from the chromatography, 1.50g (34%). TLC $R_f = 0.1$ (silica, $CHCl_3$ /hexane, 70:30). ^1H NMR ($CDCl_3$) δ 7.54 (m, 16H), 7.04 (s, 2H), 4.05 (t, 4H), 2.18 (s, 2H), 1.83 (br m, 4H), 1.64 (s, 12H), 1.51 (br m, 4H), 1.25 (br s, 56H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$) δ 153.7, 140.0,

139.8, 132.1, 132.0, 126.8, 126.7, 122.7, 122.0, 116.8, 114.0, 94.7, 87.0, 81.9, 69.6, 65.6, 31.8, 31.4, 29.6, 29.4, 26.0, 22.7, 14.1. Elem. Anal.: calcd for $C_{80}H_{106}O_4$: C, 84.90; H, 9.44; found: C, 84.55; H, 9.97.

Compounds 16b

2,5-bis-[4'-(3-hydroxy-3-methyl-1-butynyl)biphenylethynyl]-1,4-diocetadecyloxy- benzene (500 mg, 0.442 mmol) was dissolved in 10 mL of toluene and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (138 mg, 2.46 mmol) was added and the Schlenk tube that contained the solution was immersed for 5 minutes into an oil bath that had been pre-heated to 110° C. The reaction mixture was cooled and then extracted with $CHCl_3$. Evaporation of the solvent afforded compound **16b**, yield 250 mg (56%). The product was used without further purification. ^1H -NMR (300 MHz, $CDCl_3$) δ 7.54 (m, 16H), 7.04 (s, 2H), 4.05 (t, 4H), 3.17 (s, 2H), 1.83 (br m, 4H), 1.51 (br m, 4H), 1.25 (br s, 56H), 0.88 (t, 6H).

Protected Oligomer 17

5,5'-Diethynyl-2,2'-bipyridine (**10**) (0.100 g, 0.489 mmol), Compound **16** (1.0 g, 1.00 mmol), $Pd(PPh_3)_2Cl_2$ (0.021 g, 0.029 mmol) and CuI (0.011 g, 0.058 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (50 mL) and diisopropylamine (30 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 10 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with 80:20 $CHCl_3$ /hexane mixture afforded an orange solid, yield 751mg (79%). Compound **17** comes off the column as a bright fluorescent orange

band, ($R_f = 0.25$). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.83 (s, 2H), 8.44 (dd, 2H), 7.93 (dd, 2H), 7.54 (m, 16H), 7.05 (s, 4H), 4.05 (br t, 8H), 2.18 (s, 2H), 1.88 (br m, 8H), 1.64 (s, 12H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 153.9, 153.8, 153.6, 151.6, 140.0, 139.9, 139.2, 132.1, 132.0, 126.8, 126.7, 122.6, 122.0, 120.8, 120.6, 116.8, 116.7, 114.7, 113.0, 95.1, 94.7, 91.7, 90.7, 86.8, 81.9, 69.6, 69.5, 65.6, 31.9, 31.5, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; APCI MS calcd for $\text{C}_{136}\text{H}_{189}\text{N}_2\text{O}_6$ [$\text{M}+\text{H}^+$]: 1946.9; found 1946.9.

Oligomer 18

Protected oligomer **17** (600 mg, 0.308 mmol) was dissolved in 10 mL of toluene and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (138 mg, 2.46 mmol) was added and the Schlenk tube that contained the solution was immersed for 5 minutes into an oil bath that had been pre-heated to 110° C. The reaction mixture was cooled and then extracted with CHCl_3 (2 x 100 mL). Evaporation of the solvent afforded compound **18**, yield 589 mg (91%). The product was used without further purification. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.83 (s, 2H), 8.44 (dd, 2H), 7.93 (dd, 2H), 7.54 (m, 16H), 7.05 (s, 4H), 4.05 (br t, 8H), 3.15 (s, 2H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H).

Protected Oligomer 19

Oligomer **18** (0.350 g, 0.191 mmol), Compound **16** (0.391 g, 0.392 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.008 g, 0.012 mmol) and CuI (0.004 g, 0.022 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (20 mL) and diisopropylamine (10 mL) was added to the Schlenk

flask and the resulting solution was heated at 80° C for 8 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with a 70:30 CHCl₃/hexane mixture afforded **19** as an orange solid, yield 532 mg (78%). Compound **19** comes off the column as a bright fluorescent orangish/yellow band, (*R_f* = 0.30). ¹H NMR (CDCl₃) δ 8.83 (br s, 2H), 8.44 (br d, 2H), 7.93 (br d, 2H), 7.55 (br s, 32H), 7.05 (br s, 8H), 4.05 (br t, 16H), 2.18 (br s, 2H), 1.88 (br m, 16H), 1.64 (s, 12H), 1.58 (br m, 16H), 1.23 (br s, 224H), 0.87 (br t, 24H). ¹³C NMR (CDCl₃, partial) δ 154.5, 154.2, 154.1, 152.1, 140.5, 140.4, 139.6, 132.5, 127.2, 124.3, 123.2, 123.1, 122.4, 121.1, 121.0, 117.3, 116.3, 115.1, 114.5, 113.6, 111.6, 111.5, 95.5, 95.2, 95.1, 92.2, 90.9, 87.5, 87.2, 82.3, 70.0, 66.1, 32.4, 31.9, 29.9, 29.8, 26.5, 23.1, 14.5. APCI MS calcd for C₂₅₂H₃₅₇N₂O₁₀ [M+H⁺]: 3574.5; found 3574.5.

Oligomer 20

Protected oligomer **19** (500 mg, 0.140 mmol) was dissolved in 10 mL of toluene and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (63 mg, 1.12 mmol) was added and the Schlenk tube that contained the solution was immersed for 5 minutes into an oil bath that had been pre-heated to 110° C. The reaction mixture was cooled and then extracted with CHCl₃ (2 x 100 mL). Evaporation of the solvent afforded compound **20**, yield 391 mg (81%). ¹H NMR (CDCl₃) δ 8.83 (br s, 2H), 8.44 (br d, 2H), 7.93 (br d, 2H), 7.55 (br s, 32H), 7.04 (br s, 8H), 4.05 (br t, 16H), 3.15 (s, 2H), 1.88 (br m, 16H), 1.58 (br m, 16H), 1.23 (br s, 224H), 0.87 (br t, 24H).

Compound 21

1,4-Dioctadecyloxy-2,5-diiodobenzene (**6**) (2.22 g, 2.55 mmol), Pd(PPh₃)₂Cl₂ (0.054 g, 0.076 mmol) and CuI (0.029 g, 0.153 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of THF (50 mL) and diisopropylamine (50 mL) was added to the solids in the Schlenk flask. Then 2-methyl-3-butyne-2-ol (0.25 mL, 2.55 mmol) was added slowly which caused the solution to change from a pale white to a dark black color. The resulting solution was heated at 80° C for 6 hr. The reaction mixture was cooled and the solvents removed under vacuum. The crude product was purified by chromatography on silica gel with a 80:20 CHCl₃/hexane solution, yielding 803 mg (44%). The first product of the column (R_f = 1), is unreacted 1,4-diiodo-2,5-dioctadecyloxybenzene (**6**), followed by compound **21** (R_f = 0.4) and finally the bis-substituted alcohol, (R_f = 0.05). ¹H NMR (CDCl₃) δ 7.27 (s, 1H), 6.80 (s, 1H), 3.93 (t, 4H), 2.18 (s, 1H), 1.80 (br m, 4H), 1.62 (s, 6H), 1.49 (br m, 4H), 1.26 (br s, 56H), 0.88 (t, 6H). ¹³C NMR (CDCl₃) δ 154.3, 151.7, 123.7, 116.1, 112.9, 98.6, 87.4, 78.2, 70.0, 69.7, 65.7, 31.9, 31.4, 29.7, 29.4, 26.0, 22.7, 14.1. EI-MS calcd for C₄₇H₈₃IO₃: 822; found 822.

Protected Oligomer 22

5,5'-Diethynyl-2,2'-bipyridine (**5**) (0.140 g, 0.680 mmol), Compound **21** (1.15 g, 1.39 mmol), Pd(PPh₃)₂Cl₂ (0.029 g, 0.040 mmol) and CuI (0.016 g, 0.082 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of THF (60 mL) and diisopropylamine (40 mL) was added and the resulting solution was heated at 80° C for 14 hr. The solution was cooled and

the solvents removed under vacuum. Chromatography on silica gel with 80:20 hexane/ethyl ether afforded **22** as a yellow solid, yield 832 mg (77%). This product is sparingly soluble and it is necessary to be patient during chromatography, a light yellow fluorescent band which slowly comes off the column indicates compound **22**, $R_f = 0.1$. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.80 (s, 2H), 8.43 (dd, 2H), 7.92 (dd, 2H), 6.98 (s, 2H), 6.92 (s, 2H), 4.0 (m, 8H), 2.18 (br s, 2H), 1.88 (br m, 8H), 1.64 (s, 12H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 153.9, 153.7, 153.6, 151.6, 139.2, 120.7, 120.6, 116.9, 116.7, 114.0, 113.0, 99.5, 91.5, 90.4, 78.4, 69.5, 69.4, 65.7, 31.9, 31.4, 29.7, 29.3, 26.0, 22.6, 14.1; APCI MS calc'd for $\text{C}_{108}\text{H}_{173}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}^+]$: 1595.5; found 1595.5.

Oligomer 23

Protected oligomer **22** (700 mg, 0.438 mmol) was dissolved in 10 mL of toluene and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (0.196 g, 3.50 mmol) was added and the Schlenk tube that contained the solution was immersed for 5 minutes into an oil bath that had been pre-heated to 110° C. The reaction mixture was cooled and then extracted with CHCl_3 (3 x 100 mL). Evaporation of the solvent afforded compound **23**, yield 589 mg (91%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.81 (s, 2H), 8.44 (dd, 2H), 7.92 (dd, 2H), 7.01 (s, 2H), 6.99 (s, 2H), 4.01 (br t, 8H), 3.36 (s, 2H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H).

Oligomer 5-L-2

4-Bromobiphenyl (0.189 g, 0.812 mmol), Compound **23** (0.300 g, 0.203 mmol), Pd(PPh₃)₂Cl₂ (0.008 g, 0.012 mmol) and CuI (0.005 g, 0.024 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of THF (20 mL) and diisopropylamine (10 mL) was added and the resulting solution was heated at 80° C for 16 hr. At this time, TLC indicated the formation of oligomer **5-L-2**, a bright orange fluorescent band on silica gel. TLC R_f = 0.35 (silica, 70:30 CHCl₃/hexane). The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with 70:30 CHCl₃/hexane afforded **5-L-2** as a bright yellow solid, yield 246 mg (68%).

¹H-NMR (300 MHz, CDCl₃) δ 8.83 (s, 2H), 8.44 (dd, 2H), 7.93 (dd, 2H), 7.60 (m, 12H), 7.46 (t, 4H), 7.37 (d, 2H), 7.05 (s, 4H), 4.04 (br t, 8H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H). ¹³C-NMR (75.4 MHz, CDCl₃) δ 153.9, 153.8, 153.6, 151.7, 141.0, 140.3, 139.1, 132.0, 128.8, 127.6, 126.9, 122.2, 121.7, 120.8, 120.6, 116.8, 116.7, 114.8, 113.0, 95.2, 91.7, 90.6, 86.6, 69.7, 69.5, 31.9, 29.7, 29.4, 26.1, 26.0, 22.7, 14.1; APCI MS calc'd for C₁₂₆H₁₇₇N₂O₄ [M+H⁺]: 1783.6; found 1783.6.

Oligomer 5-L-3

Oligomer **18** (0.300 g, 0.164 mmol), 2-iodo-1,4-dimethoxybenzene (0.217 g, 0.820 mmol), Pd(PPh₃)₂Cl₂ (0.007 g, 0.0098 mmol) and CuI (0.004 g, 0.019 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (20 mL) and diisopropylamine (10 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 8 hr. The

solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with a 70:30 CHCl_3 /hexane mixture afforded **5-L-3** as a flaky orange solid, yield 255 mg (74%). TLC R_f = 0.40 (silica, 70:30 CHCl_3 /hexane). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.83 (s, 2H), 8.44 (dd, 2H), 7.93 (dd, 2H), 7.62 (br s, 16H), 7.06 (br s, 6H), 6.86 (br d, 4H), 4.06 (br t, 8H), 3.89 (s, 6H), 3.79 (s, 6H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 154.5, 153.9, 153.8, 153.6, 153.2, 151.6, 140.0, 139.8, 139.1, 132.2, 132.0, 126.8, 126.7, 122.7, 122.6, 120.7, 120.6, 118.0, 116.8, 116.7, 115.8, 114.7, 113.0, 112.8, 112.0, 95.1, 93.2, 91.8, 90.6, 86.8, 86.7, 69.6, 69.5, 56.5, 55.7, 31.9, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; APCI MS calcd for $\text{C}_{146}\text{H}_{193}\text{N}_2\text{O}_8$ $[\text{M}+\text{H}^+]$: 2104.0; found 2104.0.

Oligomer 5-L-4

Oligomer **20** (0.325 g, 0.094 mmol), 2-iodo-1,4-dimethoxybenzene (0.124 g, 0.470 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.004 g, 0.0056 mmol) and CuI (0.002 g, 0.011 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (20 mL) and diisopropylamine (10 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 8 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with a 60:40 CHCl_3 /hexane mixture afforded **5-L-4** as a flaky yellow solid, yield 319 mg (91%). TLC R_f = 0.50 (silica, 60:40 CHCl_3 /hexane). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.83 (br s, 2H), 8.44 (br d, 2H), 7.93 (br d, 2H), 7.62 (br s, 32H), 7.05 (br s, 10H), 6.86 (br d, 4H), 4.06 (br t, 16H), 3.90 (s, 6H), 3.80 (s, 6H), 1.88 (br m, 16H), 1.58 (br m, 16H), 1.23 (br s, 224H), 0.87 (br t, 24H). $^{13}\text{C-NMR}$

(75.4 MHz, CDCl_3 , partial) δ 154.4, 154.0, 153.8, 153.6, 153.2, 151.6, 140.1, 139.9, 139.1, 132.0, 126.8, 122.8, 122.7, 120.7, 120.6, 118.1, 116.8, 115.8, 114.7, 114.0, 113.1, 112.9, 112.1, 95.1, 94.8, 93.2, 91.8, 90.6, 87.0, 86.7, 69.4, 56.5, 55.7, 31.9, 29.7, 29.4, 26.1, 22.7, 14.1. APCI MS calcd for $\text{C}_{262}\text{H}_{361}\text{N}_2\text{O}_{12}$ $[\text{M}+\text{H}^+]$: 3730.6; found 3730.6.

Metal-Organic Oligomer **5-Re-2**

Oligomer **5-L-2** (0.100 g, 0.056 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ [75] (0.024 g, 0.067 mmol) were dissolved in 30 mL of toluene, the solution was purged with argon and then was heated at 90°C for 2 hr. The solution color changed from light yellow to deep red. During the course of the reaction the blue-green fluorescence characteristic of **5-L-2** disappeared. The solution was cooled and the toluene was removed under vacuum. The complex was purified by repeated rinsing with acetone. The metallated oligomer was obtained as a dark red solid, 107 mg (92%). ^1H -NMR (300 MHz, CDCl_3) δ 9.12 (s, 2H), 8.02 (d, 2H), 7.90 (d, 2H), 7.56 (m, 12H), 7.42 (t, 4H), 7.37 (d, 2H), 7.01 (s, 2H), 6.99 (s, 2H), 4.04 (br t, 8H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H). ^{13}C -NMR (75.4 MHz, CDCl_3) δ 196.7 (CO), 189.0 (CO), 154.7, 154.2, 153.5, 152.8, 141.0, 140.3, 140.1, 132.0, 128.8, 127.6, 126.9, 124.4, 122.9, 122.6, 122.1, 116.6, 116.3, 116.0, 111.2, 95.9, 95.5, 88.9, 86.5, 69.5, 69.4, 31.9, 29.7, 29.3, 26.1, 25.9, 22.7, 14.1; IR (KBr) 2924, 2851, 2206, 2025, 1927, 1902, 1596, 1498, 1467, 1417 cm^{-1} .

Metal-Organic Oligomer 5-Re-3

Oligomer **5-L-3** (0.100 g, 0.048 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ [75] (0.021 g, 0.057 mmol) were dissolved in 30 mL of toluene and then the solution was purged with argon and subsequently heated at 90° C for 2 hr. The solution color changed from light orange to deep red. During the course of the reaction the blue-green fluorescence characteristic of oligomer **5-L-3** disappeared. The solution was cooled and the toluene removed under vacuum, affording **5-Re-3** as a brick red solid. The complex was purified by repeated rinsing with acetone, 110 mg (96%). ^1H -NMR (300 MHz, CDCl_3) δ 9.12 (s, 2H), 8.05 (m, 4H), 7.57 (br s, 16H), 7.06 (br s, 6H), 6.83 (br d, 4H), 4.06 (br t, 8H), 3.89 (s, 6H), 3.79 (s, 6H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H). ^{13}C -NMR (75.4 MHz, CDCl_3) δ 196.7 (CO), 189.0 (CO), 154.7, 154.4, 154.1, 153.5, 153.2, 152.8, 140.2, 140.0, 139.7, 132.2, 132.1, 126.7, 126.6, 124.4, 122.9, 122.8, 122.4, 118.0, 116.6, 116.3, 115.9, 115.8, 112.8, 112.0, 111.3, 95.8, 95.4, 93.2, 89.0, 86.9, 86.8, 69.5, 69.4, 56.4, 55.7, 31.9, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; IR (KBr) 2926, 2854, 2205, 2026, 1928, 1902, 1600, 1502, 1466, 1417 cm^{-1} .

Metal-Organic Oligomer 5-Re-4

Oligomer **5-L-4** (0.100 g, 0.027 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ [75] (0.012 g, 0.032 mmol) were dissolved in 30 mL of toluene and then the solution was purged with argon and subsequently heated at 90° C for 2 hr. The solution color changed from light orange to deep red. During the course of the reaction the blue-green fluorescence characteristic of oligomer **5-L-4** disappeared. The solution was cooled and the toluene removed under vacuum, affording **5-Re-4** as a bright

red flaky solid. The complex was purified by repeated rinsing with acetone, 105 mg (96%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 9.15 (br s, 2H), 8.05 (br d, 4H), 7.61 (br s, 32H), 7.05 (br s, 10H), 6.87 (br d, 4H), 4.06 (br t, 16H), 3.90 (s, 6H), 3.80 (s, 6H), 1.88 (br m, 16H), 1.58 (br m, 16H), 1.23 (br s, 224H), 0.88 (br t, 24H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3 , partial) δ 196.7, 189.0, 154.8, 154.5, 154.2, 153.7, 153.5, 153.2, 152.8, 140.2, 140.0, 139.7, 132.2, 132.1, 126.7, 122.9, 122.7, 118.0, 116.8, 116.4, 116.0, 114.0, 112.8, 112.0, 111.3, 95.8, 94.8, 93.2, 89.0, 87.0, 86.8, 69.5, 69.4, 56.4, 55.7, 31.9, 29.7, 29.3, 26.1, 22.7, 14.1; IR (KBr) 2928, 2854, 2204, 2026, 1928, 1902, 1600, 1502, 1466, 1417 cm^{-1} .

Polymer P33

Compound **16b** (0.050 g, 0.0496 mmol), Compound **35** (0.098 g, 0.0493 mmol), $\text{Pd(PPh}_3)_4$ (0.0034 g, 0.0029 mmol), and CuI (0.0012 g, 0.0059 mmol) were placed in a Schlenk flask and degassed with Argon for 30 min. To these solids were added a degassed solution of THF (6 mL) and $(i\text{-Pr})_2\text{NH}$ (4 mL), and the mixture was heated to 80°C for 24 hr. During the course of the reaction the mixture became noticeably less fluorescent, and toward the end of the reaction, reddish material began to precipitate. The reaction was allowed to cool, and the solution was poured into 100 mL of acetone. The resulting red solid was collected via a medium frit and rinsed with hot acetone, hexane, acetonitrile and ethanol. The brick red filmy solid was allowed to dry at room temperature overnight, yielding 70 mg of **P33** (52 %). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 9.18 (br s), 8.08 (br s), 7.62 (br s), 7.0 (br s), 6.92 (br s), 4.04 (br t), 1.84 (br m), 1.56 (br

m), 1.24 (br s), 0.87 (br t). GPC (CHCl_3 , polystyrene standards) $M_n = 9.2$, $M_w = 20.2$ kD (PDI = 2.2).

CHAPTER 4

SYNTHESIS AND OPTICAL CHARACTERIZATION OF A SERIES OF PHENYLENE π -CONJUGATED OLIGOMERS

Introduction

The synthesis and characterization of the series of biphenylene oligomers provided us with a wealth of knowledge with regard to the photophysics of the oligomers and previously synthesized polymers. One of the most interesting aspects of the biphenylene work involved the conjugation break incorporated into the oligomer backbone via the twisting of the biphenyl unit. It would be of interest to replace the biphenylene unit with its planar phenylene analog, and to examine what effect this has on the photophysical properties of the oligomer. Several key questions are of interest, first, by removing the biphenyl unit, how much of a conjugation enhancement is achieved by utilizing the planar phenyl derivative? Second, what effect does this have on the relative energies of the intra-ligand $^3\pi,\pi^*$ and $^3\text{MLCT}$ excited states of the metallated oligomers? In order to answer these questions, a new series of oligomers was synthesized (Figure 4.1) along with the respective rhenium counterparts. These phenylene oligomers are composed of the same general structure as the biphenylene oligomers, i.e., a 5,5'-(2,2'-bipyridine) "core" with a conjugated network extending out, with the only difference being a change from the twisted biphenylene repeat to a more planar

phenylene backbone. A detailed description of the improved synthetic methodology used to create these oligomers and their photophysical properties is presented in this chapter.

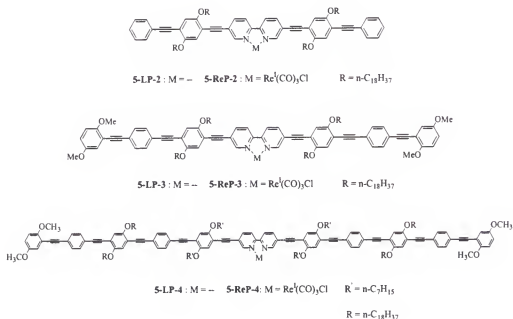


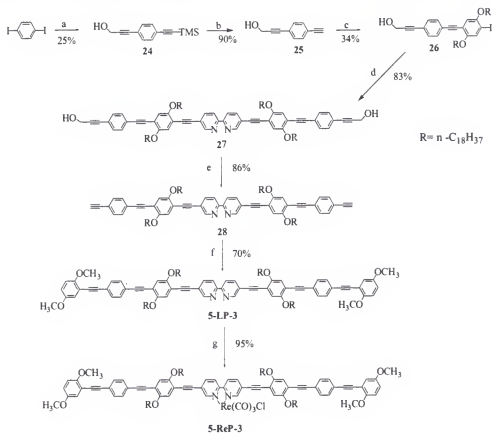
Figure 4.1: Structure of phenylene oligomers and the rhenium complexes.

Synthesis

One of the biggest problems associated with the prior methodology involved the unavoidable oxidative dimerization that would occur during the deprotection step. The high temperatures necessary to remove the tertiary alcohol proved to provide an easy route for the terminal acetylenes to dimerize, producing butadiynes. It would seem ideal to develop a similar methodology but to have a terminal protecting group that can be cleaved under more facile conditions. Godt and coworkers recently reported the use of the propargyl alcohol group in the

synthesis of a series of oligo(*para*-phenyleneethynylene)s [43]. The advantage of the propargyl alcohol protecting group is that it can easily be oxidized in the presence of MnO_2 to form the carboxylic acid which in turn is decarboxylated in situ via base to form the desired terminal acetylene.

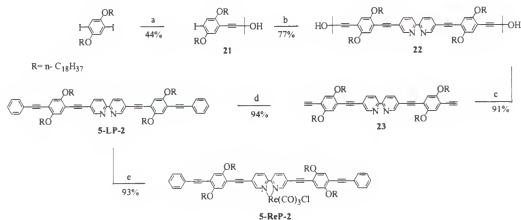
As before, 1,4-diiodobenzene was reacted with trimethylsilylacetylene (TMSA) and then with propargyl alcohol in a one-pot two step procedure to



a) 1eq. TMSA (stepwise addition), xs 2-propyn-1-ol, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, (i-Pr)₂NH; b) KOH, THF, MeOH; c) 1,4-diiodo-2,5-diiododecylbenzene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, (i-Pr)₂NH; d) 5,5'-diethynyl-2,2'-bipyridine, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, (i-Pr)₂NH; e) MnO_2 , KOH; f) 2-iodo-1,4-dimethoxybenzene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, (i-Pr)₂NH; g) $\text{Re}(\text{CO})_5\text{Cl}$, toluene.

Figure 4.2: Synthesis of phenylene derivative **5-LP-3** and **5-ReP-3**.

afford compound **24** (Figure 4.2). Again, the separation of this product is facile, owing to the polarity of the OH group of the propargyl alcohol moiety. Selective removal of the TMS group from **24** with KOH/MeOH afforded mono-protected compound **25**. Monomer **26** was obtained by coupling **25** with 1 equivalent of 1,4-diiodo-2,5-diiododecyloxybenzene. Once again, upon the preparation of large quantities of compound **26**, oligomer synthesis proceeded smoothly. Thus, reaction of 2 equivalents of **26** with 5,5'-diethynyl-2,2'-bipyridine produces



- a) 2-methyl-3-butyn-2-ol, Pd(PPh₃)₂Cl₂, CuI, THF, (i-Pr)₂NH;
 b) 5,5'-diethynyl-2,2'-bipyridine, Pd(PPh₃)₂Cl₂, CuI, THF, (i-Pr)₂NH;
 c) KOH, toluene, reflux; d) iodobenzene, Pd(PPh₃)₂Cl₂, CuI, THF, (i-Pr)₂NH; e) Re(CO)₅Cl, toluene, reflux

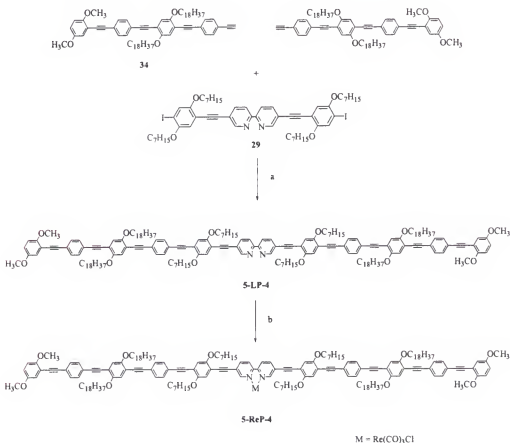
Figure 4.3: Synthesis of **5-LP-2** and **5-ReP-2**.

protected oligomer **27**, which is subsequently deprotected by MnO₂/KOH to afford **28**. Endcapping of **28** with 2-iodo-1,4-dimethoxybenzene affords **5-LP-3**, and subsequent metallation of **5-LP-3** with Re(CO)₅Cl in toluene yields **5-ReP-3**. As shown in Figure 4.3, oligomer **5-LP-2** was synthesized by a similar approach

to the one used to make **5-L-2**. Again, 1,4-diiodo-2,5-dioctadecyloxybenzene was coupled with 1 equivalent of 2-methylbut-3-yn-2-ol to produce **21**. Reaction of 2 equivalents of **21** with 5,5'-diethynyl-2,2'-bipyridine afforded **22**, which was deprotected by KOH, toluene and heat. Finally, **23** was coupled with iodobenzene to produce **5-LP-2** which is subsequently metallated to afford **5-ReP-2**.

The approach toward the synthesis of **5-LP-4** proved to be more difficult. Our initial attempt to continue the iterative sequence (ie., by reacting **28** with **26**, etc.) failed due to the inability to remove the propargyl alcohol group in the second iterative sequence. Several attempts were made, but the second generation protected oligomer was too insoluble in any solvent to allow for the deprotection. The inherent insolubility of the second generation oligomer arises from two factors. First, by increasing the molecular weight, the solubility tends to decrease, similar to the observations by Tour and coworkers [17] in their oligo(polyphenyleneethynylene) synthesis. This lack of solubility is usually attributed to the solid state ordering of these oligomers as their respective sizes increase. The second factor influencing the solubility is the presence of both propargyl alcohol protecting groups. From previous synthetic work, di-protected propargyl alcohol compounds have significantly lower solubility than their mono counterparts. In chapter 3, the tertiary diol intermediates had significantly higher solubility than the propargyl alcohol protected intermediates used in the phenylene synthesis. A new approach was deemed necessary to synthesize the

desired ligand. We choose to synthesize a two component system, one, an “outer” peripheral segment **34** (Figure 4.4) which in turn could be coupled to a central



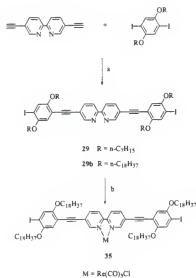
a.) $\text{Pd}(\text{PPh}_3)_4$, CuI , THF, $(i\text{-Pr})_2\text{NH}$; b.) $\text{Re}(\text{CO})_5\text{Cl}$, toluene.

Figure 4.4: Synthesis of **5-LP-4** and **5-ReP-4**.

bipyridine “core” **29**, to yield **5-LP-4**. This approach would circumvent the solubility problems associated with deprotecting the second generation oligomer, owing to the fact that the segments used to make the “outer” peripheral component would have much smaller molecular weights, and have only the

presence of one protecting group. These two factors should help ensure high solubility in solvents used for the deprotection step.

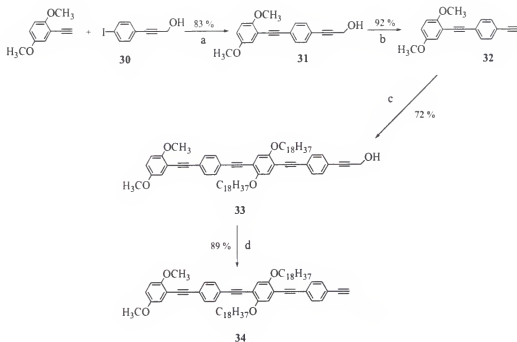
The target compound in this synthesis is the bipyridine “core” compound **29**. Reaction of 5,5'-diethynyl-2,2'-bipyridine with 2.5 equivalents of 1,4-diiodo-2,5-dioctadecyloxybenzene yields the diiodo endcapped monomer **29** in reasonable yield (Figure 4.5). The synthesis of the outer segment proved to be



a) $\text{Pd(PPh}_3)_2\text{Cl}_2$, CuI, THF, $(i\text{-Pr})_2\text{NH}$; b) $\text{Re(CO)}_5\text{Cl}$, toluene

Figure 4.5: Synthesis of “inner” bipyridine core **29**, **29b** and **35**.

much more timeconsuming (Figure 4.6) [81]. Reaction of 1,4-diiodobenzene with 1.0 equivalent of propargyl alcohol yielded compound **30**, which in turn is coupled with 2-ethynyl-1,4-dimethoxybenzene yielding protected oligomer **31**. Deprotection of **31** with MnO_2/KOH was straight forward, yielding deprotected



a) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , THF, $(i\text{-Pr})_2\text{NH}$; b) KOH , MnO_2 , CHCl_3 ;
 c) Compound **26**, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , THF, $(i\text{-Pr})_2\text{NH}$; d) KOH , MnO_2 , CHCl_3 .

Figure 4.6: Synthesis of the “outer” segment used in the synthesis of **5-LP-4**.

compound **32**. Coupling of compound **32** with monomer **26** yielded the protected oligomer in excellent yield, compound **33**. Further deprotection to **34** afford our desired “peripheral” segment without difficulty. Coupling of diiodo monomer **29** with the end segment **33** proceeded smoothly, yielding **5-LP-4** in excellent yield (Figure 4.4). Finally, **5-LP-4** was metallated with $\text{Re}(\text{CO})_5\text{Cl}$ in toluene to yield **5-ReP-4**.

UV-Visible Absorption Spectra

Figure 4.7 compares the UV-visible absorption spectra of the free oligomers with those of the corresponding (L)Re(CO)₃Cl complexes, where L = oligomer. The oligomers again feature two intense absorptions in the 300 – 500 nm region, again corresponding to a long-axis and short-axis polarized π, π^* transition. It is important to note that contrary to the biphenylene derivatives, the phenylene oligomers exhibit a further red-shift in the absorption maxima (396 – 414 nm) for the low energy π, π^* transition. This is consistent with a more planar backbone owing to the planar phenylene moiety. Rhenium complexes **5-ReP-2** – **5-ReP-4** exhibit similar bands in the UV-visible compared to the free ligand, with the noticeable difference that a significant red-shift is observed for the long-axis polarized transition along with a smaller red-shift for the short-axis polarized transition. Again this red-shift of the long-axis transition is associated with increasing the central chromophore length induced by metallation, similar to that observed in the biphenylene derivatives. The extinction coefficients for the free oligomers and metal complexes are given in Table 4.1 and 4.2, respectively.

Emission Spectroscopy

Oligomers **5-LP-2** – **5-LP-4** all exhibit strong fluorescence in the blue region of the spectra, as shown in Figure 4.8. This fluorescence is very similar to that observed for the biphenylene derivatives, with a small but noticeable blue-shift for the phenylene compounds. The radiative decay rates are very high for these oligomers, with each oligomer possessing a high quantum yield (Φ_f), listed

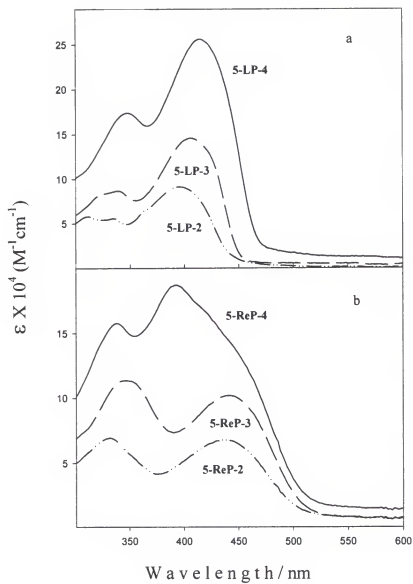


Figure 4.7: Absorption spectra of (a) 5-LP-2 – 5-LP-4 and (b) 5-ReP-2 – 5-ReP-4. Spectra are acquired on THF solutions at 298 K.

in Table 4.1. The emission lifetimes for oligomers **5-LP-2** – **5-LP-4** are very short (~ 1 ns), again consistent with the biphenylene derivatives. It is important to note that no phosphorescence was observed for any of these oligomers.

The rhenium complexes **5-ReP-2** – **5-ReP-4** exhibit no noticeable fluorescence. The rhenium complexes exhibit a weak low energy emission that increases with decreasing temperature, similar to that observed in the biphenylene derivatives. Luminescence spectra were recorded at varying temperatures ranging from 298 K to 80 K, as shown in Figure 4.9. Lifetimes for the low-energy emission maximum for the complexes are given in Table 4.2.

Time Resolved Infrared Spectroscopy

Compounds **5-ReP-2** – **5-ReP-4** all exhibit weak TRIR spectra that are consistent with the lowest excited state being of $^3\pi,\pi^*$ nature. Figure 4.10 illustrates the ground state IR and excited-state difference IR absorbance spectra of **5-ReP-3**, which is typical for the phenylene series. In the TRIR spectrum, the sharp, ground –state $\nu(\text{CO})$ band at 2023 cm^{-1} appears as a bleach with a new excited state band appearing at 2005 cm^{-1} . The lower energy CO bands, 1927 and 1906 cm^{-1} appear both as a bleach along with a new broad excited state absorption centered at 1896 cm^{-1} respectively.

Discussion

The objective of this work is to closely examine and compare the photophysics of the biphenylene derivatives to their phenylene counterparts. The key difference between the two series of compounds clearly revolves around the

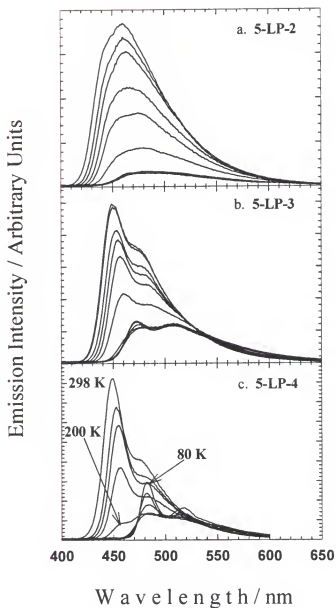


Figure 4.8: Emission spectra of 5-LP-2 – 5-LP-4 in 2-MTHF solutions (350 nm excitation) at various temperatures ranging from 298 to 80 K. Emission intensity decreases with decreasing temperature except as noted, and the spectra are in 30 K increments. (a) 5-LP-2; (b) 5-LP-3; (c) 5-LP-4 (note unique low temperature trends).

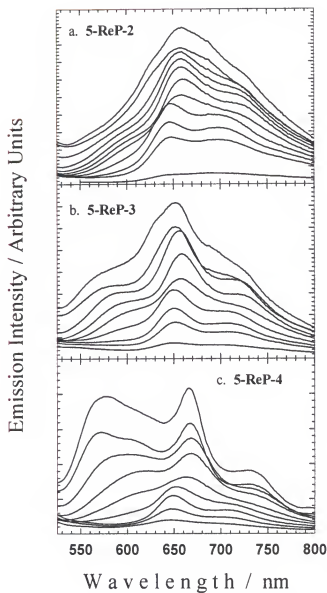


Figure 4.9: Emission spectra of **5-ReP-2** – **5-ReP-4** in 2-MTHF solutions (450 nm excitation) at various temperatures ranging from 298 to 80 K. Emission intensity increases with decreasing temperature, and spectra are in 30 K increments. (a) **5-ReP-2**; (b) **5-ReP-3**; (c) **5-ReP-4**.

Table 4.1: Photophysical Properties of Phenylene Oligomers.^a

Oligomer	$\lambda_{\max}$ abs / nm ($\epsilon_{\max} / \text{M}^{-1} \text{cm}^{-1} 10^4$)	Assignment	$\lambda_{\max}^{b,c}$ em / nm 298 K	Φ_{em}^d 298 K	$\tau_{\text{em}}^{b,e} / \text{ns}$ 298 K
5-LP-2	334 (5.45)	π, π^*	460	0.72	1.0
	396 (5.40)	π, π^*			
5-LP-3	338 (7.93)	π, π^*	449	0.77	0.91
	406 (9.80)	π, π^*			
5-LP-4	334 (12.7)	π, π^*	452	0.87	0.63
	414 (25.6)	π, π^*			

^aTHF solutions at 298K. ^b Samples are argon degassed. ^cMaximum of fluorescence band. ^d Fluorescence quantum yields measured by using actinometers as described in text. ^e Fluorescence decay lifetimes.

Table 4.2: Photophysical Properties of Phenylene Rhenium Complexes.^a

Complex	$\lambda_{\text{max}} \text{ abs} / \text{nm}$ ($\epsilon_{\text{max}} / \text{M}^{-1} \text{cm}^{-1} 10^4$)	Assignment	$\lambda_{\text{max}}^{\text{b}} \text{ em} / \text{nm}$ 298 K	$\tau_{\text{em}}^{\text{c}} / \text{ns}$ 298 K	$E_{1/2}^{\text{red}} / \text{V vs. SCE}$
5-ReP-2	331 (6.51)	π, π^*	659	123	-0.79 ^d
	438 (6.78)	π, π^*			
5-ReP-3	348 (10.8)	π, π^*	650	181	-0.79 ^e
	442 (10.2)	π, π^*			
5-ReP-4	338 (14.7)	π, π^*	646	164	-0.82 ^e
	393 (18.7)	π, π^*			

^aTHF solutions at 298K. ^bMaximum of MLCT band, samples are argon degassed. ^cEmission decay of MLCT excited state. ^dPt disc working electrode. ^eGCE disc working electrode. ^fNo resolvable wave was obtained for **5-ReP-4**.

planarity of the oligomer backbone. It was shown in the previous chapter that the photophysics of the biphenylene derivatives were controlled by the relative conjugation length of the oligomer. This is most apparent in the UV-visible spectrum, where an initial shift to lower energy (370 – 400 nm) of the π, π^* absorption is noted for **5-L-1** to **5-L-2**. Any additional conjugation enhancement that would result from further iterations results in little to no change in the position of the π, π^* absorption, notably the band-position only changes from 404 - 406 nm for oligomers **5-L-3** and **5-L-4**. Similar trends were also observed with the rhenium complexes. By removing the conjugation break (biphenyl unit) from the backbone of the oligomer, it is anticipated that the effective conjugation length will increase as the size of the oligomer increases. The increase in conjugation length is measured by the absorption maximum, which is expected to shift towards the red until the conjugation length is fully developed.

Careful comparison of a series of different substituted PPE polymers and their respective UV-visible spectra should provide some insight into what defines the effective conjugation length of the **5-LP** oligomers. A series of different substituted PPE polymers and their optical properties presented by Bunz [39] show some interesting trends. Dialkyl substituted PPEs (**P1**) typically show a prominent absorption centered between 384 – 388 nm (Figure 4.11a) [82]. If every second benzene ring is substituted by alkoxy groups (**P2**), this absorption shifts further to the red with an absorption band centered at 410 – 414 nm (figure 4.11b) [83], while the fully alkoxy-substituted PPEs (**P3**) (two alkoxy groups

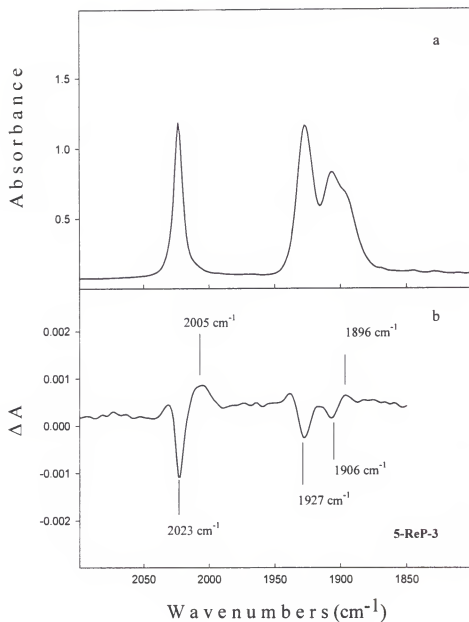


Figure 4.10: Ground state (a) and 600 ns time-resolved infrared difference spectra (b) for **5-ReP-3** in CH_2Cl_2 at 298 K following 354.7 nm excitation.

per benzene ring) display their transition at 442 – 452 nm (Figure 4.11c) [84]. Lower absorbance values for these different PPE polymers typically indicate very short polymers, in which the convergence length is not yet reached. Based on the similarities in structure of the phenyl-dialkoxybenzene PPE (**P2**) and the **5-LP** oligomers, it is anticipated that the conjugation length of the higher **5-LP** oligomers will eventually be centered around 410 – 414 nm. The possibility exists that the spectra of the **5-LP** oligomers will be slightly blue-shifted from **P2** due to the lack of planarity of the 2,2'-bipyridine ring as described earlier.

Similar to the trends observed for the biphenylene derivatives, metallation of the **5-LP** oligomers should red-shift the lowest energy π, π^* transition of the **5-LP** oligomers. The red-shift of the π, π^* transition is associated with increasing the conjugation length throughout the oligomer backbone caused by the metal forcing the 2,2'-bipyridine rings from a “transoid” like to a planar “cisoid” conformation necessary to bind the metal.

Of primary interest though is the effect that the increased conjugation length will have on the relative ordering of states of the rhenium complexes. From the previous biphenylene work, it was concluded that a very small energy gap existed between the $^3\pi, \pi^*$ state of the oligomer backbone and the $^3\text{MLCT}$ excited state. By replacing the biphenylene unit with a phenylene unit, the backbone becomes easier to oxidize, by nearly 100 mV. By altering the energy of the $^3\pi, \pi^*$ intra-ligand state it may be possible to lower it below the energy of the $^3\text{MLCT}$ excited state, allowing for us to clearly assign a portion of the

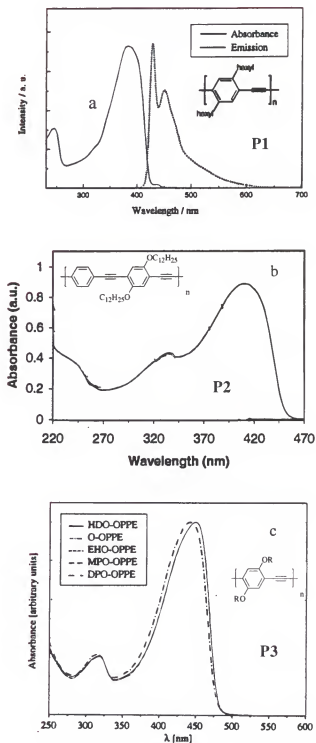


Figure 4.11: Absorption spectra of (a) Dialkyl substituted PPE (Ref. 82) (b) Phenyl-dialkoxybenzene substituted (Ref. 83) and (c) Dialkoxy substituted PPE (Ref. 84).

emission spectra to phosphorescence, which we were unable to do with the biphenylene derivatives with certainty.

UV-Visible Absorption Spectra

A gradual red-shift for the π, π^* transition for oligomers **5-LP-2** - **5-LP-4** was observed. One point to note is that each further iteration used to make the **5-LP-2** - **5-LP-4** oligomers consistently results in an increase in the conjugation length by 8 nm. Further attempts to synthesize higher phenylene oligomers were thwarted due to synthetic difficulties and time constraints. By careful comparison of the absorption spectrum of the structurally similar PPE polymer **P2**, it is doubtful whether further iterations to form larger phenylene oligomers would have resulted in any further red-shifting of the oligomer's absorption maximum. This is illustrated by the fact that the UV-visible spectrum of **P2** (figure 4.11b) is very similar to the absorption spectrum of **5-LP-4** (Figure 4.7a). The similarities in structure and absorption properties between the two compounds provides some insight into the effective conjugation length of **P2**. By comparison to **5-LP-4**, the spectral trends seem to suggest that the effective conjugation length of **P2** is at most 6 repeat units (Figure 4.12), which is an upper limit owing to the fact that the nonplanar 2,2'-bipyridine is slightly disturbing the conjugation. The two different series of oligomers, **5-L** and **5-LP** respectively, have quite different absorption properties, owing to the increased conjugation length of the **5-LP** series. The absorption properties of the metallated oligomers, **5-Re** and **5-ReP**,

are quite similar. These same spectral features seem to indicate the existence of a central inorganic component along with an outer organic chromophore. This seems to strongly suggest that the inner metal chromophore is nearly identical in the phenylene and biphenylene derivatives.

5-LP-4

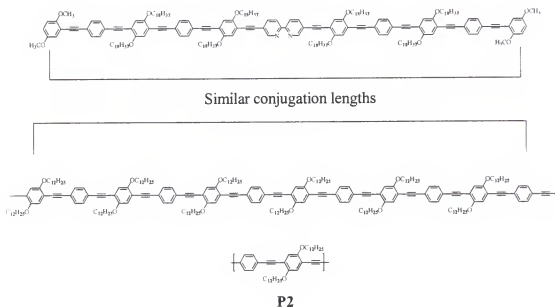


Figure 4.12: Comparison of the relative conjugation lengths of **P2** and **5-LP-4**.

Emission Spectra

The emission spectra of oligomers **5-LP-2** - **5-LP-4** are similar but subtly different than the **5-L** series. The emission spectra of **5-L-2** and **5-LP-2** are consistent with the fact that there is very little structural difference between the compounds. Of interest is the fact that the emission maxima for the **5-LP** series in general is blue-shifted by 5 nm compared to the **5-L** series. This implies that the

$^1\pi,\pi^*$ excited state of the **5-LP** series is higher in energy. This is interesting in that the absorption trends in the phenylene derivatives (more delocalized excited state) are opposite to what one would expect from the emission spectra (higher energy). This discrepancy is consistent with the **5-LP** oligomers having a smaller Stokes shift relative to the **5-L** oligomers. Again, the quantum efficiencies (Φ_f) are high for the **5-LP** series of oligomers, again similar to the **5-L** series. The main difference though is that in the **5-L** series, the quantum yields decrease throughout the series from **5-L-1** – **5-L-4**. This is opposite from the **5-LP** series, where the quantum yields increase as the size of the oligomer increases. The higher quantum yields for the **5-LP** series is consistent with the oligomers having a higher $^1\pi,\pi^*$ excited state energy. What is interesting though is the fact that the quantum yields in the **5-LP** series increases throughout the series, opposite to that of the **5-L** oligomers. By increasing the delocalization along the oligomer backbone in the **5-LP** oligomers, one should increase the ϕ_{isc} and subsequently decrease the fluorescence quantum yields (ϕ_{em}). One possible explanation for the increased quantum yields is a gradual increase in the radiative decay rate (k_r) throughout the **5-LP** oligomers. An increased radiative decay rate might result from increased delocalization throughout the oligomer backbone associated with the increased number of chromophores in solution for the larger oligomers.

As in the biphenylene work, the emission properties of the **5-ReP** complexes are of primary interest. The low-energy room temperature emission spectra of the **5-ReP** series are again very weak ($\Phi_f < 10^{-4}$) again very similar to the biphenylene derivatives. As the temperature is lowered, the emission intensity

increases, again consistent with either phosphorescence or MLCT emission. The emission spectra of the rhenium complexes appears to consist of two components. One component is a structureless band (570 – 600 nm) that blue-shifts as the temperature decreases, and the other is a structured band (650 nm) that remains fixed as the temperature decreases. The structureless band increases in intensity with increasing oligomer size, leading to a clear separation of the two emission bands in **5-ReP-4**. Due to the temperature independence of the 650 nm band, it is assigned to $^3\pi,\pi^*$ phosphorescence from the oligomer backbone, while the broad structureless band is assigned to $^3\text{MLCT}$ emission. This is consistent with the fact that the emission maximum for phosphorescence is typically temperature independent, while the energy of the $^3\text{MLCT}$ state is highly temperature dependent. Little change was observed in the band structure of the emission spectra between the **5-Re** and **5-ReP** series, except for the notable fact that the $^3\text{MLCT}$ luminescence emission intensity is much higher for the phenylene derivatives. This may be due to the increased rigidity of the all phenylene backbone, subsequently lowering the non-radiative decay pathways and increasing the $^3\text{MLCT}$ emission. The room temperature lifetimes of **5-ReP-2** – **5-ReP-4** are all clearly indicative of luminescence from $^3\text{MLCT}$ excited state. The emission spectra of these compounds is dominated by a two-component decay (Table 4.3). One component dominates the spectra with a large amplitude which either consists of fluorescence impurities from trace amounts of free ligand, or fluorescence resulting from aggregation of the complexes. A second weaker component exists with a longer lifetime, with the lifetime varying based on the

Table 4.3: Variable temperature emission decay times of the **5-ReP** complexes.

Complex ^a	T/K	550 nm Emission			650 nm Emission				
		α_1	τ_1 / ns	α_2	τ_2 / ns	α_1	τ_1 / ns	α_2	τ_2 / ns
5-ReP-2	298	0.999	0.476	0.001	375.4	0.996	0.476	0.004	255.0
	171	0.999	0.202	0.001	56.4	0.996	4.961	0.004	2644
	80	0.999	0.202	0.001	91.5	0.995	4.961	0.005	2801
5-ReP-3	298	0.999	0.200	0.001	86.8	0.995	1.85	0.005	754.7
	172	0.999	0.200	0.001	48.9	0.995	10.0	0.005	3657
	80	0.997	0.200	0.003	7.36	0.997	10.0	0.003	5097
5-ReP-4	298	-	-	-	-	0.996	0.74	0.004	176.9
	80	1	1.10	-	-	>0.999	1.10	<0.001	b

^a2-THF solutions; 405 nm excitation. ^bDecay component was too weak to accurately measure the lifetime.

band position. The critical point is that the 550 nm emission has a lifetime around 100 ns, while the 650 nm emission has a significantly longer lifetimes, in the micro-second time region. Although the lifetime of the 650 nm emission is still somewhat short for phosphorescence, it is not unreasonably short.

Time-Resolved InfraRed Spectroscopy

By applying time-resolved techniques our hope was to elucidate the electronic structure and excited state ordering in our CO-containing rhenium phenylene complexes. Analysis of two different rhenium compounds that exhibit different TRIR difference spectra lend support to our assignment of the lowest lying excited state of the rhenium complexes being of intra-ligand triplet nature [85]. Ground state and transient infrared difference spectra for *fac*-[Re(phen)(CO)₃(4-Mepy)]⁺ (4-Mepy is 4-methylpyridine, phen is 1,10-phenanthroline) in the $\nu(\text{CO})$ region is shown in Figure 4.13a. In this spectrum, the broad, ground-state $\nu(\text{CO})$ band at 1931 cm^{-1} appears as a bleach with new-excited state bands appearing at 1965 and 2015 cm^{-1} [86, 87]. The broad band in the ground state actually consists of two overlapping $\nu(\text{CO})$ bands. They are resolved in the excited state because reduction at phen to give phen^{•-}, decreases the local electronic symmetry. In the ground state the three facially pyridyl-type ligands are electronically similar. In the MLCT excited state phen becomes phen^{•-}, distinct from 4-Mepy. The third $\nu(\text{CO})$ band at 2036 cm^{-1} also shifts to higher energy (2065 cm^{-1}) in the excited state. The shifts to higher energy are consistent with partial oxidation of the Re^I to Re^{II} and formation of the

Re^{II} (phen $^{-}$) excited state. The energies of the $\nu(\text{CO})$ bands increase because of the decrease in the Re-CO backbonding to Re^{II} . This increases the triple bond character of the CO ligands.

The transient infrared difference spectrum for *fac*-[Re(dppz)(CO)₃(PPh₃)]⁺* (dppz is dipyrdo[3,2-a:2,2'-c]phenazine) is shown in figure 4.13b. In this case the three $\nu(\text{CO})$ bands in the excited state are only slightly shifted and the shifts are to lower energy. The transient spectrum can be simulated qualitatively by assuming that the $\nu(\text{CO})$ bands in the excited state are slightly broadened and decreased in energy by ca. 5 cm⁻¹ in the excited state. There is no evidence for bands at higher energy characteristic of a MLCT excited state. The relatively small shifts in $\nu(\text{CO})$ in the dppz complex is consistent with a ligand-localized excited state which is slightly electron donating at the metal relative to the ground state dppz. For the dppz complex this is a lowest-lying, dppz-based $^3\pi, \pi^*$ state. In the **5-ReP** complexes the $\nu(\text{CO})$ bands shift to lower energy, similar to the *fac*-[Re(dppz)(CO)₃(PPh₃)]⁺ complex. This shift again is consistent with a ligand-localized excited state, the $^3\pi, \pi^*$ excited state of the oligomer.

Conclusion

The primary objective of this work was oriented at addressing the excited state properties of the biphenylene derivatives. The previous work on the biphenylene derivatives left us with many questions as to the true nature of the low energy emission in the rhenium complexes. It was believed that the low energy emission of the rhenium complexes was a contribution from $^3\pi, \pi^*$

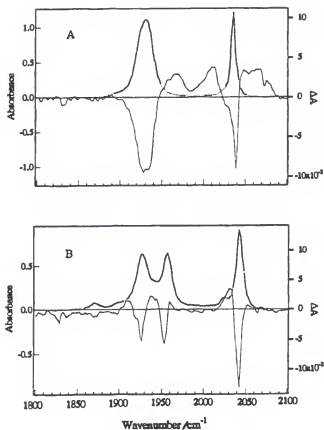


Figure 4.13: (a) Ground state (broken curve) and 600 ns times-resolved infrared difference spectra of $fac\text{-[Re(phen)(CO)}_3\text{(4-Mepy)]}^+$ (phen is 1,10-phenanthroline; 4-Mepy is 4-methylpyridine) (b) compared to $fac\text{-[Re(dppz)(CO)}_3\text{(PPh}_3\text{)]}^+$ (dppz is dipyrido[3,2-a:2,2'-c]phenazine) [85].

phosphorescence from the oligomer backbone along with luminescence from a $^3\text{MLCT}$ excited state, although we had little spectroscopic evidence to prove this. In order to address this question, the synthesis of a new series of oligomers, the phenylene derivatives was undertaken. It was envisioned that by increasing the planarity of the oligomer backbone, the relative energies of the $^3\pi,\pi^*$ and $^3\text{MLCT}$

excited states might be perturbed enough to allow for spectral assignments. Most notably, by lowering the oxidation potential of the oligomer backbone, the energy of the $^3\pi,\pi^*$ state should also be lowered. At first, the synthetic methodology to create the phenylene derivatives failed, but a new iterative approach was developed to form the largest oligomer, **5-LP-4**. A detailed analysis was undertaken on the photophysical properties of the oligomers **5-LP-2** – **5-LP-4** and their rhenium complexes **5-ReP-2** – **5-ReP-4**. The absorption properties of the phenylene derivatives proved as expected, with the energy of the $^1\pi,\pi^*$ transition shifting to lower energy as the conjugation length increased, indicating a more planar backbone for the phenylene derivatives relative to their biphenyl counterparts. The emission properties of the rhenium complexes **5-ReP-2** – **5-ReP-4** are quite interesting, with a resolvable dual component system. One higher energy component (550 nm) is attributed to ^{3} MLCT luminescence while a lower energy sharp band (650 nm) is the result of phosphorescence from the triplet state of the oligomer backbone. Time resolved infrared spectroscopic studies also confirm the role of the $^3\pi,\pi^*$ intra-ligand excited state as the energetically lowest lying transition.

Experimental

Photophysical Measurements

All sample solutions studied are either in THF or 2-MTHF (2-methyl-tetrahydrofuran) solutions. All photophysical studies were conducted in 1 cm quartz cuvettes. All room temperature studies were conducted on Argon bubble degassed solutions, and all low temperature studies were conducted on solvent

glasses degassed by four freeze-pump-thaw cycles (ca. 10^{-4} Torr). For the absorption and emission studies, sample concentrations were adjusted to produce optically dilute solutions (i.e., $A < 0.20$ at all wavelengths).

Absorption spectra were collected on either an HP8452A diode-array or Varian Cary 100 dual-beam spectrometer. Corrected steady state emission measurements were conducted on a SPEX F-112 fluorimeter. Emission quantum yields were measured relative to 9,10-dicyanoanthracene ($\Phi_{\text{em}} = 0.89$) and perylene ($\Phi_{\text{em}} = 0.89$) in ethanol [62]. Time-resolved emission decays were observed with time-correlated single photon counting (FLT, Photochemical Research Associates; Excitation filter/source: Schott UG-11/H₂ spark (350 nm maximum) or 405 nm IBH NanoLED-07 laser diode; Emission filter 450 and 550 nm (**5-LP** oligomers) or 600 nm (**5-ReP** complexes) interference filters). Lifetimes were determined by the observed decays with DECAN fluorescence lifetime deconvolution software [73]. Low temperature emission measurements were conducted in 1 cm glass tubes contained in an Oxford Instruments cryostat connected to an Omega CYC3200 automatic temperature controller.

General Synthetic

Diisopropylamine was distilled from KOH and tetrahydrofuran was distilled from sodium benzophenone ketyl and stored under argon. The synthesis of 2-ethynyl-1,4-dimethoxybenzene [74] and compounds **21-23** are described in chapter 3. Copper(I) iodide, Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, 4,4'-diiodobenzene and propargyl alcohol were purchased from Aldrich Chemical Co. and used without further purification. Activated MnO₂ was purchased from Fischer and used

without further purification. Trimethylsilylacetylene and 2-methyl-3-butyne-2-ol were obtained from GFS chemicals and used without further purification. All cross-coupling reactions using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Pd}(\text{PPh}_3)_4$ were carried out under standard Schlenk and vacuum line techniques.

Synthesis

Compound 24

1,4-Diiodobenzene (9.33 g, 28.2 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (595 mg, 0.847 mmol) and CuI (323 mg, 1.70 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of trimethylsilylacetylene (4.0 mL, 28.2 mmol), tetrahydrofuran (45 mL) and diisopropylamine (30 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 3 hr. Heavy ammonium iodide salt formed immediately. After 3 hr 2-propyne-1-ol (4.7 mL, 85.0 mmol) was added. The solution turned from light yellow to dark black and heating was continued for an additional 6 hr. The solution was allowed to cool and after evaporation of the solvent the product was chromatographed on silica gel with chloroform affording **24** as a white solid, (R_f = 0.4), 1.70 g (25%). ^1H NMR (CDCl_3) δ 7.37 (dd, 4H), 4.50 (d, 2H), 1.80 (t, 1H), 0.26 (s, 9H). ^{13}C NMR (CDCl_3) δ 131.8, 131.4, 123.2, 122.5, 104.4, 96.3, 89.0, 85.3, 51.6, -0.13. EI-MS calcd for $\text{C}_{14}\text{H}_{16}\text{OSi}$: 228; found 228.

Compound 25

Methanol (20 mL), tetrahydrofuran (40 mL), and a 20% NaOH (5 mL) solution were added to **24** (1.50 g, 6.5 mmol) and the resulting solution was stirred rapidly. The mixture, which immediately became viscous, was stirred at

room temperature for 5 hr. The reaction mixture was diluted with 100 mL of water and extracted with 200 mL of CHCl_3 . The organic layer was separated, dried and the solvent evaporated leaving a tan solid which was used without further purification, 923 mg (90%). ^1H NMR (CDCl_3) δ 7.41 (dd, 4H), 4.50 (d, 2H), 3.16 (s, 1H), 1.70 (t, 1H). ^{13}C NMR (CDCl_3) δ 131.8, 131.4, 122.9, 122.1, 89.1, 85.0, 83.0, 78.9, 51.6. EI-MS calcd for $\text{C}_{11}\text{H}_8\text{O}$: 156; found 156.

Compound 26

Compound **25** (1.0 g, 6.40 mmol), 1,4-diiodo-2,5-dioctadecyloxybenzene (5.54 g, 6.40 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.134 g, 0.192 mmol) and CuI (0.073 g, 0.384 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of THF (50 mL) and diisopropylamine (50 mL) was added to the solids and the resulting solution was heated to 80°C and stirred for 3 hr. After evaporation of the solvents, the crude solid was purified by chromatography on silica gel with 80:20 CHCl_3 /hexane affording 1.95 g of **26** (34%). TLC $R_f = 0.3$ (silica, CHCl_3 /hexane, 80:20). The first product off of the column ($R_f = 1$), is the non-polar unreacted 1,4-diiodo-2,5-dioctadecyloxybenzene (**6**), followed by a pale yellow band, compound **26** ($R_f = 0.3$). ^1H NMR (CDCl_3) δ 7.41 (dd, 4H), 7.30 (s, 1H), 6.88 (s, 1H), 4.50 (dd, 2H), 3.98 (m, 4H), 1.83 (br m, 4H), 1.70 (t, 1H), 1.51 (br m, 4H), 1.25 (br s, 56H), 0.88 (t, 6H). ^{13}C NMR (CDCl_3) δ 154.3, 151.8, 131.8, 131.5, 123.8, 123.3, 122.5, 115.6, 113.3, 95.2, 93.7, 87.8, 87.4, 81.8, 70.0, 69.8, 51.6, 31.9, 31.4, 29.7, 29.4, 26.0, 22.7, 14.1. EI-MS calcd for $\text{C}_{53}\text{H}_{83}\text{IO}_3$: 895; found 895.

Protected Oligomer 27

5,5'-Diethynyl-2,2'-bipyridine (0.110 g, 0.541 mmol), **26** (1.0 g, 1.11 mmol), Pd(PPh₃)₂Cl₂ (0.023 g, 0.032 mmol) and CuI (0.012 g, 0.065 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (30 mL) and diisopropylamine (10 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 10 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with 80:20 CHCl₃/hexane mixture afforded an orange solid, yield 780 mg (83%) (R_f = 0.25, fluorescent blue orange band). ¹H-NMR (300 MHz, CDCl₃) δ 8.82 (dd, 2H), 8.44 (dd, 2H), 7.92 (dd, 2H), 7.45 (dd, 8H), 7.04 (s, 2H), 7.02 (s, 2H), 4.50 (d, 4H), 3.98 (t, 8H), 1.88 (br m, 8H), 1.70 (t, 2H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H). ¹³C-NMR (75.4 MHz, CDCl₃) δ 154.0, 153.7, 153.5, 151.6, 139.9, 131.1, 130.9, 128.6, 128.4, 123.4, 122.3, 120.6, 116.8, 116.6, 114.4, 94.7, 92.8, 89.1, 88.9, 87.8, 85.3, 69.5, 51.6, 31.9, 31.5, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; APCI MS calcd for C₁₂₀H₁₇₃N₂O₆ [M+H⁺]: 1738.3; found 1738.3.

Oligomer 28

Protected oligomer **27** (500 mg, 0.287 mmol) was dissolved in 60 mL of chloroform and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (160 mg, 2.87 mmol) and MnO₂ (249 mg, 2.87 mmol) were added and the solution was stirred under argon at room temperature for 3 hr. The solution was then passed through a coarse 3 cm frit of silica gel to remove the MnO₂. The chloroform was then removed under vacuum, yielding 415 mg of a yellow solid (86 %). This compound was used without further

purification. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.82 (dd, 2H), 8.43 (dd, 2H), 7.92 (dd, 2H), 7.47 (s, 8H), 7.04 (s, 2H), 7.02 (s, 2H), 4.05 (t, 8H), 3.18 (s, 2H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H).

Compound 29

5,5'-Diethynyl-2,2'-bipyridine (0.100 g, 0.490 mmol), 1,4-diheptoxy-2,5-diiodobenzene (0.681 g, 1.22 mmol), $\text{Pd(PPh}_3)_2\text{Cl}_2$ (0.020 g, 0.029 mmol) and CuI (0.011 g, 0.058 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (20 mL) and diisopropylamine (60 mL) was added to the Schlenk flask and the resulting solution was heated at 80°C for 10 hr. The solution was cooled and the solvents removed under vacuum. The solid was dissolved in a minimal amount of hexane, and dry packed on a 6 cm column of silica gel. The resulting column was flushed with 1 L of hexane, removing the excess 1,4-diheptaoxy-2,5-diiodobenzene. The solvent polarity was increased to a 10% chloroform/hexane solution and the column eluted with 200 mL of this solvent mixture. A small non-fluorescent yellow band began to move down the column. The solvent polarity was then increased to a 30/70 chloroform/hexane mixture and the yellow band collected, yielding 100 mg of compound **29** (25%). It is very important not to collect any of the other yellow bands that follow the initial one, these bands contain dimer products. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.82 (s, 2H), 8.48 (d, 2H), 7.91 (d, 2H), 7.31 (s, 2H), 6.92 (s, 2H), 4.04 (br t, 8H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.30 (br s, 24H), 0.87 (br t, 12H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 155.2, 152.7, 151.9, 145.5, 142.0, 129.8,

124.5, 121.8, 116.5, 115.8, 105.9, 89.5, 80.1, 70.9, 70.6, 32.5, 30.0, 26.8, 23.4,
14.9. FAB-MS Calcd. For $C_{45}H_{25}N_2O_3I_2$ 926.24, found 926.30.

Compound 29b

5,5'-Diethynyl-2,2'-bipyridine (0.100 g, 0.490 mmol), 1,4-diiodo-2,5-diiodo- decyloxybenzene (1.06 g, 1.22 mmol), $Pd(PPh_3)_2Cl_2$ (0.020 g, 0.029 mmol) and CuI (0.011 g, 0.058 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (30 mL) and diisopropylamine (70 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 12 hr. The solution was cooled and the solvents removed under vacuum. The solid was dissolved in a minimal amount of hexane, and dry packed on a 6 cm column of silica gel. The resulting column was flushed with 1 L of hexane, removing the excess 1,4-diiododecyloxy-2,5-diiodobenzene. The solvent polarity was increased to a 10% chloroform/hexane solution and the column eluted with 200 mL of this solvent mixture. A small non-fluorescent yellow band began to move down the column. The solvent polarity was then increased to a 40/60 chloroform/hexane mixture and the yellow band collected, yielding 125 mg of compound **29b** (15%). It is very important not to collect any of the other yellow bands that follow the initial one, these bands contain dimer products. ^1H -NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 2H), 8.41 (d, 2H), 7.91 (dd, 2H), 7.32 (s, 2H), 6.92 (s, 2H), 4.04 (m, 8H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.30 (br s, 112H), 0.87 (br t, 12H). ^{13}C -NMR (75.4 MHz, $CDCl_3$) δ 154.9, 152.8, 152.0, 145.3, 141.9, 129.6, 124.5, 121.8, 116.3, 116.0, 105.9, 89.5, 80.1, 70.9,

70.6, 31.5, 29.7, 29.3, 26.1, 26.0, 22.3, 14.0. FAB-MS Calcd. For $C_{98}H_{158}N_2O_4I_2$ 1682.1, found 1682.2.

Compound 30

1,4-Diiodobenzene (5.0 g, 0.015 mol), $Pd(PPh_3)_2Cl_2$ (315 mg, 0.450 mmol) and CuI (171 mg, 0.90 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of 2-methyl-3-butyne-2-ol (1.0 mL, 0.015 moles), tetrahydrofuran (50 mL) and diisopropylamine (30 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 3 hr. Heavy ammonium iodide salt formed immediately. The solution was allowed to cool and after evaporation of the solvent the product was chromatographed on silica gel with 80:20 $CHCl_3$ /hexane affording **30** as a white solid, yield 1.59 g (41%). The first product that elutes off the column (R_f = 1), is unreacted 4,4'-diiodobenzene, followed by compound **30** (R_f = 0.3) and finally the bis-substituted diol, (R_f = 0.1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, 2H), 7.12 (d, 2H), 4.46 (s, 2H), 2.48 (s, 1H). ^{13}C -NMR (75.4 MHz, $CDCl_3$) δ 137.4, 133.1, 121.9, 94.5, 88.6, 84.6, 51.4. EI-MS calcd for C_9H_7IO : 258; found 258.

Compound 31

2-Ethynyl-1,4-dimethoxybenzene (1.0 g, 6.20 mmol), compound **30** (1.60 g, 6.20 mmol), $Pd(PPh_3)_2Cl_2$ (131 mg, 0.186 mmol) and CuI (71 mg, 0.372 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of tetrahydrofuran (15 mL) and diisopropylamine (15 mL) was then added and the solution was heated at 80° C for 12 hr. The solution was then allowed to cool to room temperature and the solvents removed under vacuum.

The resulting crude red solid was chromatographed on silica gel with 60:40 CHCl_3 /hexane solution affording **31** as a tan solid, $R_f = 0.35$ (83%). ^1H NMR (300 MHz, CDCl_3) δ 7.48 (d, 2H), 7.39 (d, 2H), 7.03 (d, 1H), 6.84 (m, 2H), 4.48 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 2.48 (br s, 1H). ^{13}C -NMR (75.4 MHz, CDCl_3) δ 154.4, 153.1, 131.7, 131.5, 123.4, 122.2, 117.9, 115.9, 112.5, 112.0, 92.8, 88.9, 87.5, 85.2, 56.4, 55.7, 51.5. EI-MS calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3$: 292; found 292.

Compound 32

Compound **31** (500 mg, 1.71 mmol) was dissolved in 60 mL of chloroform and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (160 mg, 2.87 mmol) and MnO_2 (249 mg, 2.87 mmol) was added and the solution was stirred under argon at room temperature for 3 hr. The solution was then passed through a 3 cm frit of silica gel to remove the MnO_2 . The chloroform was then removed under vacuum, yielding 412 mg of a yellow solid (92%). This compound was used without further purification. ^1H -NMR (300 MHz, CDCl_3) δ 7.46 (d, 2H), 7.37 (d, 2H), 7.03 (d, 2H), 6.84 (m, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.17 (s, 1H). EI-MS calcd for $\text{C}_{18}\text{H}_{14}\text{O}_2$: 262; found 262.

Compound 33

Compound **32** (0.350 g, 1.33 mmol), compound **26** (1.20 g, 1.33 mol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (28 mg, 0.04 mmol) and CuI (15.1 mg, 0.08 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (20 mL) and diisopropylamine (10 mL) was added to the Schlenk flask and the resulting solution was heated at 80°C for 16 hr. The solution was cooled and

the solvents removed under vacuum. Chromatography on silica gel with 60:40 CHCl_3 /hexane mixture afforded a yellow solid, yield 889 mg (72%), $R_f = 0.25$. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.48 (m, 8H), 7.04 (d, 1H), 7.0 (d, 2H), 6.86 (m, 2H), 4.50 (d, 2H), 4.02 (t, 4H), 3.88 (s, 3H), 3.78 (s, 3H), 1.83 (br m, 4H), 1.54 (br m, 4H), 1.25 (br s, 56H), 0.88 (t, 6H). $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 154.5, 153.9, 153.8, 153.2, 131.8, 131.6, 131.3, 131.2, 123.5, 123.2, 121.8, 117.9, 116.5, 116.4, 115.9, 113.9, 113.7, 112.6, 112.0, 104.7, 96.2, 94.7, 94.5, 93.1, 88.0, 87.8, 87.6, 87.3, 71.9, 56.5, 55.8, 39.6, 31.4, 29.7, 26.0, 22.7, 14.1. APCI MS calc'd for $\text{C}_{63}\text{H}_{93}\text{O}_5$ $[\text{M}+\text{H}^+]$: 929.4; found 929.4.

Compound 34

Compound 33 (700 mg, 0.753 mmol) was dissolved in 50 mL of chloroform and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (300 mg, 7.53 mmol) and MnO_2 (450 mg, 7.53 mmol) was added and the solution was stirred under argon at room temperature for 1 hr. This deprotection took slightly longer than the typical small molecule analogs. The progress of the deprotection can be easily monitored by TLC, R_f (33) = 0.25 and R_f (34) = 1.0 in a 60:40 CHCl_3 /hexane mixture. The solution was then passed through a 3 cm coarse frit of silica gel to remove the MnO_2 . The chloroform was then removed under vacuum, yielding 602 mg of a yellow solid, (89%). This compound was used without further purification. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.50 (m, 8H), 7.04 (d, 1H), 7.0 (d, 2H), 6.86 (m, 2H), 4.02 (t, 4H), 3.88 (s, 3H), 3.79 (s, 3H), 3.18 (s, 1H), 1.83 (br m, 4H), 1.54 (br m, 4H), 1.25 (br s, 56 H), 0.88 (t, 6H).

Compound 35

Compound **29b** (100 mg, 0.0594 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ [53] (26 mg, 0.0713) were dissolved in 10 mL of toluene, the solution was purged with argon and then was heated at 90°C for 2 hr. The solution color changed from light yellow to deep red. The solution was allowed to cool and the solvent was removed under reduced pressure. The crude red solid was rinsed with excess hexane and acetone, yielding 108 mg of a brick red solid (92%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 9.11 (s, 2H), 8.04 (dd, 4H), 7.37 (s, 2H), 6.92 (s, 2H), 4.03 (m, 8H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.30 (br s, 112H), 0.87 (br t, 12H).

Oligomer 5-LP-2

Iodobenzene (0.138 g, 0.677 mmol), compound **23** (refer to chapter 3) (0.200 g, 0.135 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.006 g, 0.008 mmol) and CuI (0.003 g, 0.016 mmol) were combined in a Schlenk flask which was then purged with argon. A degassed mixture of THF (10 mL) and diisopropylamine (5 mL) was added and the resulting solution was heated at 80°C for 16 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with 80:20 CHCl_3 /hexane afforded **5-LP-2** as a yellow solid ($R_f = 0.3$), this product elutes off the column as a highly fluorescent blue, yellow band, yield 205 mg (94%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.83 (dd, 2H), 8.44 (d, 2H), 7.93 (dd, 2H), 7.54 (m, 4H), 7.35 (m, 6H), 7.04 (s, 4H), 4.04 (br t, 8H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 153.9, 153.7, 153.5, 151.6, 139.1, 131.6, 128.3, 123.3, 121.7, 120.8, 120.6, 116.8, 116.6, 114.7, 113.0, 95.2, 91.8, 90.5, 85.8, 69.6, 69.5, 31.9, 29.7, 29.4,

26.1, 26.0, 22.7, 14.1; APCI MS calc'd for $C_{114}H_{169}N_2O_4$ $[M+H]^+$: 1630.3; found 1630.3.

Oligomer 5-LP-3

Oligomer **28** (0.250 g, 0.148 mmol), 2-iodo-1,4-dimethoxybenzene (0.197 g, 0.744 mmol), $Pd(PPh_3)_2Cl_2$ (0.006 g, 0.008 mmol) and CuI (0.003 g, 0.016 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (20 mL) and diisopropylamine (10 mL) was added to the Schlenk flask and the resulting solution was heated at $80^\circ C$ for 8 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with a 70:30 $CHCl_3$ /hexane mixture afforded **5-LP-3** as a flaky orange solid ($R_f = 0.3$), the product eluted off as a bright highly fluorescent blue, orange band, yield 202 mg (70%). ^1H -NMR (300 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.44 (dd, 2H), 7.93 (dd, 2H), 7.53 (d, 8H), 7.04 (br s, 6H), 6.86 (br d, 4H), 4.05 (br t, 8H), 3.89 (s, 6H), 3.79 (s, 6H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); ^{13}C -NMR (75.4 MHz, $CDCl_3$) δ 154.0, 153.6, 153.2, 153.1, 152.7, 151.2, 138.9, 138.7, 131.1, 130.9, 122.8, 122.6, 120.2, 120.1, 117.6, 116.3, 115.5, 113.9, 112.7, 112.2, 111.6, 94.6, 92.7, 91.4, 90.0, 87.3 (overlapping peak), 69.1, 56.0, 55.4, 31.5, 29.7, 29.3, 26.1, 26.0, 22.3, 14.0; APCI MS calcd for $C_{134}H_{185}N_2O_8$ $[M+H]^+$: 1950.4; found 1950.4.

Oligomer 5-LP-4

Compound **34** (0.200 gr, 0.222 mmoles), compound **29** (0.103 gr, 0.111 mmoles) and $Pd(PPh_3)_4$ (15.4 mg, 0.013 mmoles) were combined in a Schlenk flask and degassed with argon. To these solids was added a degassed solution of

tetrahydrofuran (10 mL) and diisopropylamine (5 mL) and the solution was heated at 80°C for 24 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with a 60:40 CHCl₃/hexane mixture afforded **5-LP-4** as a flaky orange solid ($R_f = 0.30$), the oligomer eluted off the column as a highly fluorescent blue, orange band, yield 184 mg (59%). ¹H-NMR (300 MHz, CDCl₃) δ 8.83 (s, 2H), 8.44 (dd, 2H), 7.93 (dd, 2H), 7.53 (br s, 16H), 7.04 (br s, 10H), 6.86 (br d, 4H), 4.05 (br t, 16H), 3.89 (s, 6H), 3.79 (s, 6H), 1.88 (br m, 16H), 1.58 (br m, 16H), 1.23 (br s, 136H), 0.88 (br t, 24H); ¹³C-NMR (75.4 MHz, CDCl₃, partial) δ 154.5, 153.6, 153.2, 131.6, 131.5, 131.4, 131.3, 123.3, 123.2, 123.1, 118.0, 116.8, 116.6, 115.9, 113.9, 113.8, 112.6, 112.0, 95.0, 94.8, 94.7, 93.1, 92.4, 88.0, 87.8, 87.6, 69.6, 56.4, 55.8, 31.8, 29.7, 29.3, 29.0, 26.0, 22.6, 14.1. APCI MS calcd for C₁₉₄H₂₅₇N₂O₁₂ [M+H⁺]: 2810.1; found 2810.1.

Metal-Organic Oligomer 5-ReP-2

Oligomer **5-LP-2** (0.100 g, 0.061 mmol) and Re(CO)₅Cl [75] (0.026 g, 0.073 mmol) were dissolved in 20 mL of toluene, the solution was purged with argon and then was heated at 90°C for 2 hr. The solution color changed from light yellow to deep red. During the course of the reaction the blue-green fluorescence characteristic of **5-LP-2** disappeared. The solution was cooled and the toluene was removed under vacuum. The complex was purified by repeated rinsing with acetone. The metallated oligomer was obtained as a dark red solid, yield 109 mg (93%). ¹H-NMR (300 MHz, CDCl₃) δ 9.12 (s, 2H), 8.02 (dd, 4H), 7.54 (m, 4H), 7.35 (m, 6H), 7.00 (s, 4H), 4.04 (br t, 8H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); ¹³C-NMR (75.4 MHz, CDCl₃) δ 196.7

(CO), 189.0 (CO), 154.9, 154.1, 153.4, 152.8, 140.1, 131.6, 128.4, 128.3, 124.5, 123.2, 122.8, 116.7, 116.4, 116.0, 111.2, 95.9, 95.4, 88.8, 85.7, 69.6, 69.4, 31.9, 29.7, 29.3, 26.1, 25.9, 22.7, 14.1; IR (KBr) 2924, 2851, 2206, 2025, 1927, 1902, 1596, 1498, 1467, 1417 cm^{-1} .

Metal-Organic Oligomer 5-ReP-3

Oligomer **5-LP-3** (0.100 g, 0.051 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ [75] (0.022 g, 0.062 mmol) were dissolved in 30 mL of toluene and then the solution was purged with argon and subsequently heated at 90°C for 2 hr. The solution color changed from light orange to deep red. During the course of the reaction the blue-green fluorescence characteristic of oligomer **5-LP-3** disappeared. The solution was cooled and the toluene removed under vacuum, affording **5-ReP-3** as a brick red solid. The complex was purified by repeated rinsing with acetone, yield 109 mg (95%). ^1H -NMR (300 MHz, CDCl_3) δ 9.12 (s, 2H), 8.03 (dd, 4H), 7.54 (br s, 8H), 7.04 (br s, 6H), 6.86 (br d, 4H), 4.05 (br t, 8H), 3.89 (s, 6H), 3.79 (s, 6H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); ^{13}C -NMR (75.4 MHz, CDCl_3) δ 196.7 (CO), 189.0 (CO), 154.9, 154.5, 154.1, 153.5, 153.2, 152.9, 140.2, 131.6, 131.5, 124.5, 123.5, 122.8, 122.7, 118.0, 116.6, 116.4, 115.9, 115.7, 112.6, 112.0, 111.5, 95.7, 95.4, 93.0, 89.0, 87.8, 87.5, 69.5, 69.4, 56.4, 55.7, 31.9, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; IR (KBr) 2926, 2854, 2205, 2026, 1928, 1902, 1600, 1502, 1466, 1417 cm^{-1} .

Metal-Organic Oligomer 5-ReP-4

Oligomer **5-LP-4** (0.100 g, 0.035 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ [75] (0.015 g, 0.042 mmol) were dissolved in 30 mL of toluene and then the solution was

purged with argon and subsequently heated at 90⁰ C for 2 hr. The solution color changed from light orange to deep red. During the course of the reaction the blue-green fluorescence characteristic of oligomer **5-LP-4** disappeared. The solution was cooled and the toluene removed under vacuum, affording **5-ReP-4** as a red solid. The complex was purified by repeated rinsing with acetone, yield 103 mg (95%). ¹H-NMR (300 MHz, CDCl₃) δ 9.12 (s, 2H), 8.03 (dd, 4H), 7.53 (br s, 16H), 7.04 (br s, 10H), 6.86 (br d, 4H), 4.05 (br t, 16H), 3.89 (s, 6H), 3.79 (s, 6H), 1.88 (br m, 16H), 1.58 (br m, 16H), 1.23 (br s, 136H), 0.88 (br t, 24H); ¹³C-NMR (75.4 MHz, CDCl₃, partial) δ 197.5, 155.1, 154.5, 154.2, 153.6, 153.5, 153.2, 153.0, 140.2, 131.6, 124.6, 123.5, 123.3, 123.0, 122.9, 122.6, 117.9, 116.8, 116.5, 116.0, 115.8, 114.0, 113.7, 112.7, 112.0, 111.6, 95.6, 95.2, 94.8, 94.7, 93.1, 88.9, 88.1, 87.9, 70.4, 57.3, 56.6, 32.7, 29.8, 26.8, 23.5, 14.5; IR (KBr) 2926, 2854, 2205, 2026, 1928, 1902, 1600, 1502, 1466, 1417 cm⁻¹.

CHAPTER 5

SYNTHESIS AND OPTICAL CHARACTERIZATION OF A SERIES OF 4,4'-BIPHENYLENE π -CONJUGATED OLIGOMERS

Introduction

The 5,5'-biphenyl and phenyl oligomers provided a wealth of knowledge with regard to the optical properties of structurally similar PPE based polymers and oligomers. By resonance, substitution at the 5,5'-positions of bipyridine allows for the most efficient electronic communication between the two organic segments. One drawback to the “para” substitution on the bipyridine rings is that the bipyridine nitrogens are “meta” to the conjugated segment. This “meta” substitution hampers the electronic communication between the metal center and the organic backbone. By substituting in the 4,4'-position of the bipyridine ring we might be able to actually reverse this effect. Substitution in the 4,4'-position should serve to break the conjugation in the organic backbone, for the organic segments are now “meta” to each other, but at the same time increase the electronic communication between the metal center and the organic backbone. The advantage of this is that it might allow for better excited state resolution between the metal and ligand based states. In this chapter the synthesis of a series of 4,4'-biphenyl oligomers (Figure 5.1) is presented as well as their optical properties.

Synthesis

The key compound in the synthesis of the 4-L series of oligomers is 4,4'-dibromo-2,2'-bipyridine (**39**). The synthesis of compound **39** described by Woodward and co-workers proved difficult to reproduce [88]. Although the synthetic pathway used (Figure 5.2) was identical, the workup conditions were quite different for several of the key intermediates, typically involving

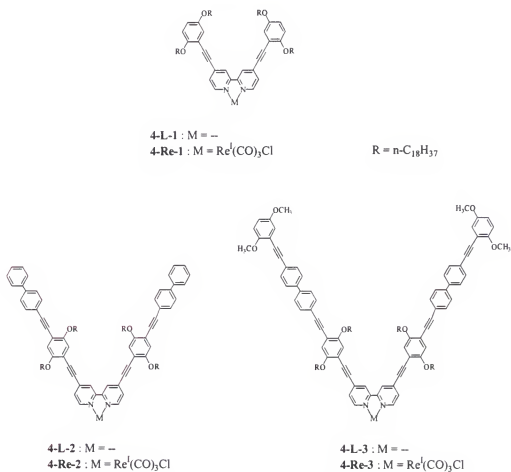
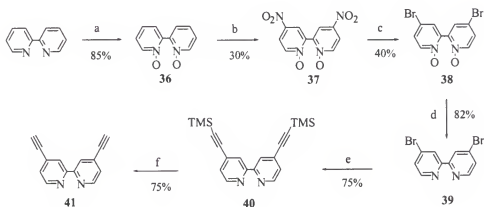


Figure 5.1: Structures of 4,4'-oligomers and metal complexes.

different extraction procedures, full details are described in the synthetic section. Reaction of 2,2'-bipyridine with H_2O_2 formed N,N'-dioxide **36** in excellent yield.

Further nitration of compound **36** with fuming nitric acid yielded **37** without difficulty. Bromination of **37** was accomplished by refluxing compound **37** in acetic acid with acetyl bromide, yielding **38**. Deoxygenation of compound **38** with PBr_3 in chloroform yielded the target compound **39**. A procedure from Sessler and co-workers was applied to synthesize the desired end product, 4,4'-diethynyl-2,2'-bipyridine [89]. First, compound **39** was reacted with TMSA



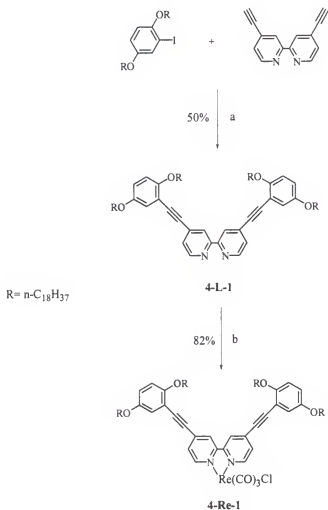
a) 30% H_2O_2 , Δ ; b) HNO_3 (fuming), H_2SO_4 , Δ ; c) acetyl bromide, Δ ; d) PBr_3 , Δ ; e) TMSA, $\text{Pd}(\text{PPh}_3)_4$, CuI , CH_3CN , triethylamine, Δ ; f) KOH , THF, CH_3OH .

Figure 5.2: Synthesis of 5,5'-diethynyl-2,2'-bipyridine

under typical Sonogashira coupling conditions, followed by deprotection with base to afford the desired product, **41**.

Once compound **41** was available in large quantities, the synthesis of the **4-L** compounds proceeded quickly. Reaction of 2-iodo-1,4-dioctadecyloxybenzene with 0.5 equivalents of **41** gave oligomer **4-L-1** without difficulty, subsequent metallation with $\text{Re}(\text{CO})_5\text{Cl}$ yielded **4-Re-1** (Figure 5.3). The synthesis of **4-L-2** required a slightly different approach than that used for the **5-L**

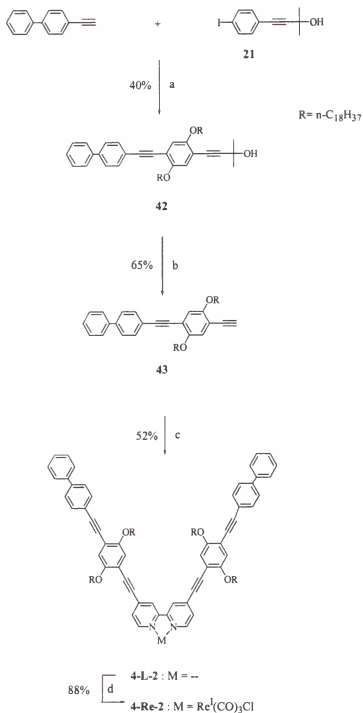
series (Figure 5.4). Reaction of compound **21** with 1 equivalent of 4-ethynylbiphenyl yielded compound **42** in excellent yield. Deprotection of



a) Pd(PPh₃)₂Cl₂, CuI, THF, (i-Pr)₂NH; b) Re(CO)₅Cl, toluene, Δ

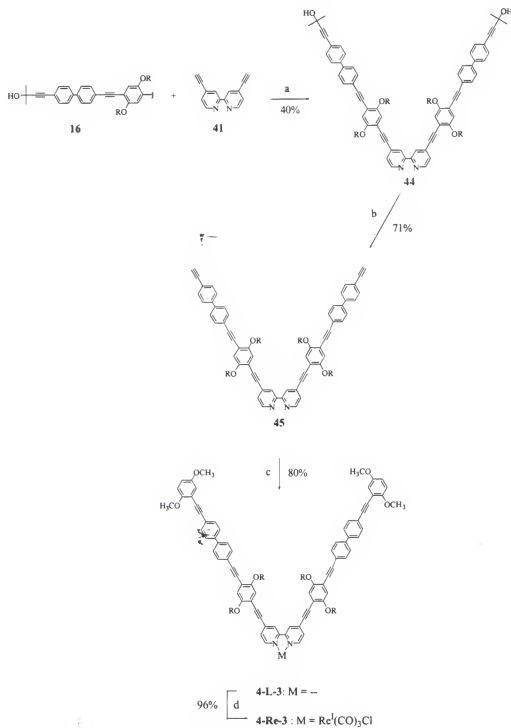
Figure 5.3: Synthesis of **4-L-1** and **4-Re-1**

oligomer **42** with base under refluxing toluene yielded the terminal acetylene compound **43**. Further reaction of 2.0 equivalents of **43** with 4,4'-dibromo-2,2'-bipyridine yielded the desired end product, **4-L-2**. Metallation of **4-L-2** with



a) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , THF, $(i\text{-Pr})_2\text{NH}$; b) KOH , toluene, Δ ; c) 0.5 equivalents compound 39, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , THF, $(i\text{-Pr})_2\text{NH}$; d) $\text{Re}(\text{CO})_5\text{Cl}$, toluene, Δ .

Figure 5.4: Synthesis of **4-L-2** and **4-Re-2**.



- a) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , THF, $(i\text{-Pr})_2\text{NH}$; b) KOH , toluene, Δ ;
 c) 2-iodo-1,4-dimethoxybenzene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , THF, $(i\text{-Pr})_2\text{NH}$;
 d) $\text{Re}(\text{CO})_5\text{Cl}$, toluene, Δ .

Figure 5.5: Synthesis of **4-L-3** and **4-Re-3**.

$\text{Re}(\text{CO})_5\text{Cl}$ to afford **4-Re-2** proved facile. Formation of **4-L-3** followed the identical methodology used for the **5-L** series (Figure 5.5). Reaction of compound **16** with 0.5 equivalents of compound **41** under palladium coupling conditions yielded protected oligomer **44** in excellent yield. Deprotection of **44** under basic conditions to yield the unprotected oligomer **45** proceeded smoothly. Further reaction of oligomer **45** with 2-iodo-1,4-dimethoxybenzene gave **4-L-3** in reasonable yield. Metallation of **4-L-3** with $\text{Re}(\text{CO})_5\text{Cl}$ to afford **4-Re-3** again proved trivial.

UV-Visible Absorption Spectra

Figure 5.6 compares the UV-visible absorption spectra of the free oligomers with those of the corresponding $(\text{L})\text{Re}(\text{CO})_5\text{Cl}$ complexes, where L = oligomer. The oligomers again feature two intense π, π^* absorptions in the 300 – 500 nm region, very similar to the **5-L** and **5-LP** oligomers. One point to mention is that the absorption maxima of the **4-L** series is blue-shifted by nearly 20 nm relative to the biphenyl and phenylene oligomers. Also similar to the **5-L** and **5-LP** series is the fact that the π, π^* absorption exhibits a significant red-shift between **4-L-1** and **4-L-2** but does not exhibit any further red-shifting for the larger oligomer **4-L-3**. This is not surprising owing to the fact that the conjugated backbone structures are identical between the **4-L** and **5-L** series. Absorption maxima and absorptivities for the **4-L** series are listed in Table 5.1.

The **4-Re-1** – **4-Re-3** complexes exhibit π, π^* absorption bands that are very similar to those of the **5-Re** and **5-ReP** series, with the notable difference that the **4-Re** series experiences a 20 nm blue-shift relative to there **5-Re** and

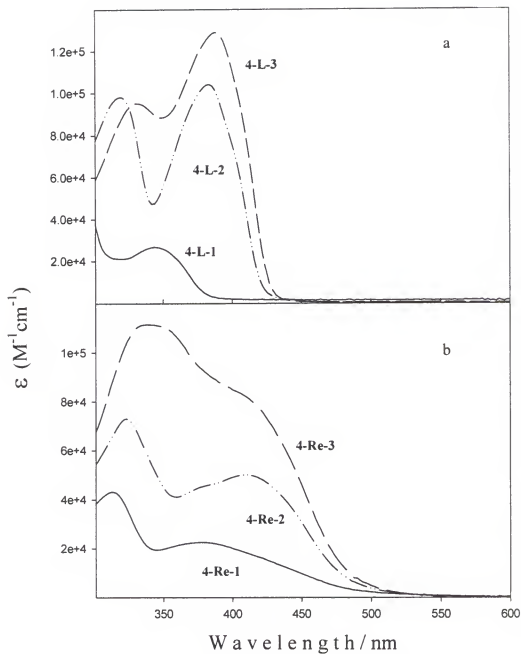


Figure 5.6: Absorption spectra of (a) 4-L-1 – 4-L-3 and (b) 4-Re-1 – 4-Re-3. Spectra are acquired on THF solutions at 298 K.

Table 5.1: Photophysical Properties of Free Oligomers.^a

Oligomer	λ_{max} abs / nm ($\epsilon_{\text{max}} / \text{M}^{-1} \text{cm}^{-1} 10^4$)	Assignment	$\lambda_{\text{max}}^{\text{b,c}}$ em / nm 298 K	$\lambda_{\text{max}}^{\text{b,c}}$ em / nm 80 K	$\Phi_{\text{em}}^{\text{d}}$ 298 K	$\tau_{\text{em}}^{\text{b,e}}$ / ns
4-L-1	296 (4.56)	π, π^*	415	430, 614	0.77	1.31
	346 (2.67)	π, π^*				
4-L-2	320 (9.84)	π, π^*	422	427, 614	0.91	1.46
	384 (10.4)	π, π^*				
4-L-3	332 (9.51)	π, π^*	426	433	0.96	1.15
	388 (12.9)	π, π^*				

^aTHF solutions at 298K. ^b Samples are argon degassed. ^cMaximum of fluorescence band. ^dFluorescence quantum yields measured by using actinometers as described in text, values are erroneously high, see text for details. ^eFluorescence decay lifetimes.

Table 5.2: Photophysical Properties of Rhenium Complexes.^a

Oligomer	$\lambda_{\max}$ abs / nm ($\epsilon_{\max} / \text{M}^{-1} \text{cm}^{-1} \cdot 10^4$)	Assignment	$\lambda_{\max}^{\text{b,c}}$ em / nm 298 K	$\lambda_{\max}^{\text{b,c}}$ em / nm 80 K	$\Phi_{\text{em}}^{\text{d}}$ 298 K	$\tau_{\text{em}}^{\text{b,e}} / \text{ns}$
4-Re-1	314 (4.31) 378 (2.25)	π, π^* π, π^*	670	610	0.0032	37
4-Re-2	324 (7.30) 408 (5.00)	π, π^* π, π^*	678	609	0.0044	183
4-L-3	340 (11.1) 408 (8.25)	π, π^* π, π^*	615	621	0.0046	330

^a2-MTHF solutions at 298K and 80 K. ^bSamples are argon degassed. ^cMaximum of emission band. ^dEmission quantum yields measured by using actinometers as described in text. ^eTA decay lifetimes.

5-ReP counterparts. This blue-shift in the low energy π, π^* absorption band seems to imply that the central chromophore length in the **4-Re** series is smaller than that in the **5-Re** and **5-ReP** series. Another significant point is that the absorptivities of the lower energy band in the **4-Re** complexes increases as the conjugation length increases. Absorption maxima and absorptivities for the **4-Re** series are listed in Table 5.2.

Emission Spectroscopy

Oligomers **4-L-1** – **4-L-3** all exhibit strong fluorescence in the blue region of the visible, as shown in Figure 5.7. This fluorescence is very similar to that observed for the **5-L** and **5-LP** oligomers. The radiative decay rates are very high for these oligomers, with each oligomer possessing a high quantum yield (Φ_f), listed in Table 5.1. The emission lifetimes for oligomers **4-L-1** – **4-L-3** are very short (~ 1.5 ns), and notably longer than the **5-L** and **5-LP** oligomers. It is important to note that phosphorescence was observed for the **4-L-1** and **4-L-2** oligomers at low temperatures ($T < 200$ K).

The rhenium complexes **4-Re-1** – **4-Re-3** exhibit no noticeable fluorescence. The rhenium complexes exhibit a weak low energy emission that increases with decreasing temperature, similar to that observed in the **5-L** and **5-LP** derivatives. Luminescence spectra were recorded at varying temperatures ranging from 298 K to 80 K, as shown in Figure 5.8. Lifetimes for the low-energy emission maxima for the complexes are given in Table 5.2. Although the quantum efficiencies were low, emission intensities of the **4-Re** series were large enough to accurately measure, and values are listed in Table 5.2.

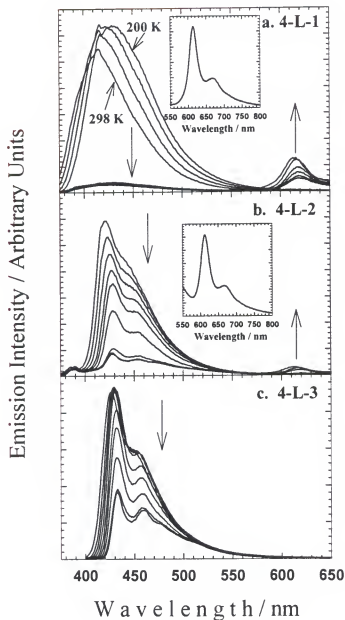


Figure 5.7: Emission spectra of oligomers **4-L-1** – **4-L-3** in 2-MTHF solutions (350 nm excitation) at various temperatures ranging from 298 to 80 K. The emission intensity trends as a function of temperature are indicated by the arrows, individual spectra are in 30 K increments. Inset spectra show 80 K phosphorescence. (a) **4-L-1**; (b) **4-L-2**; (c) **4-L-3**.

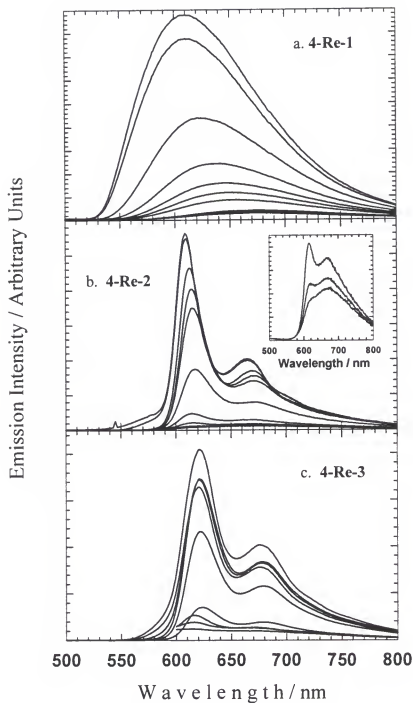


Figure 5.8: Emission spectra of **4-Re-1** – **4-Re-3** in 2-MTHF solutions (400 nm excitation) at various temperatures ranging from 298 to 80 K. Emission intensity increases with decreasing temperature, and spectra are in 20 K increments for all complexes except **4-Re-3**, which is in 30 K increments.

Discussion

The goal of this work is to closely compare the photophysics of the “linear” **5-L** and **5-LP** complexes with those of the “bent” **4-L** series. To gain a better understanding of what is expected with meta substitution, a careful comparison between the photophysical properties of a series of meta and para substituted PPE polymers might provide us with some useful information. The critical areas to focus on in the comparison of a series of meta and para linked PPE polymers are their respective differences in absorption and emission spectra as well as the changes in their lifetimes and fluorescence quantum yields.

A series of meta and para linked PPE polymers (Figure 5.9) presented by Swager [1] and Pang [83] clearly illustrates the conjugation break incorporated in the polymer backbone due to the meta linkage. The absorption maximum shifts from 428 nm for polymer **PPEP1** to 388 nm for polymer **PPEM1**. This blue-shift indicates a higher excited state energy for **PPEM1**. Similar results obtained by Pang confirms this conjugation break where the absorption spectrum (Figure 5.10a) of **PPEP2** was red-shifted by 36 nm compared to **PPEM2**. These results imply a shorter conjugation length in the meta linked polymers **PPEM1** and **PPEM2**. It is interesting to note that the absorption spectrum of **PPEM2** is nearly identical to the model compound **MC1**. This leads one to believe that the effective conjugation length of **PPEM2** is merely a few repeat units. This is contrary to polymers **PPEP1** and **PPEP2** where the conjugation length is known to extend through 10-15 repeat units [90]. Based on these results it is expected

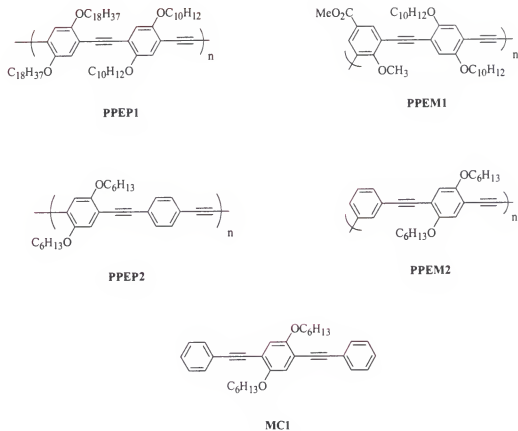


Figure 5.9: Meta and para linked polymers studied by Swager [1] and Pang [83].

that the absorption spectra of the 4-L oligomers will be significantly bluer than their 5-L and 5-LP counterparts. This blue-shifting results from the oligomers having a much shorter conjugation length due to the conjugation break resulting from “meta” substitution on the bipyridine ring.

The trends in the emission spectra between the meta and para linked polymers should follow their absorption properties. It is anticipated that the higher

energy absorption bands in the meta linked polymers will result in a higher energy emission band. This is clearly evident when one compares the band positions of **PPEP2** with **MC1** and **PPEM2**, where the fluorescence maximum of **PPEP2** is 40 nm red-shifted from that of **PPEM2** (Figure 5.10b). It is also noted that the emission spectrum of **PPEM2** is very similar to that of **MC1**, indicating the presence of similar pathways for radiative decay. The similarity in both absorption and emission characteristics of **PPEM2** and **MC1** suggest that the

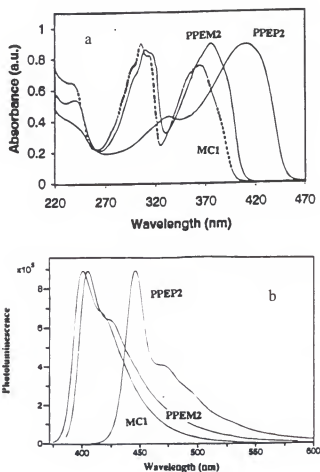


Figure 5.10: (a) UV-visible spectra of **PPEP2**, **PPEM2** and **MC1** in THF solutions at 298 K [1, 83]. (b) Normalized fluorescence spectra of PPEs in THF solutions at 298 K [83].

Table 5.3: Photophysical Properties of PPE Polymers and Model Compound.^a

Oligomer	λ_{max} abs / nm ($\epsilon_{\text{max}} / \text{M}^{-1} \text{cm}^{-1} \cdot 10^4$)	Assignment	$\lambda_{\text{max}}^{\text{b,c}}$ em / nm 298 K	$\Phi_{\text{em}}^{\text{d}}$ 298 K	$\tau_{\text{em}}^{\text{b,e}} / \text{ns}$ 298 K	Ref
PPEP1	428 (3.6)	π, π^*	459	0.76	0.66	1
PPEP2	411	π, π^*	458	0.45	-----	61
PPEM1	388 (3.5)	π, π^*	418	0.50	1.31	1
PPEM2	375	π, π^*	418	0.44	-----	61
MC1	368	π, π^*	414	0.66	-----	61

^aTHF solutions at 298K. ^bSamples are argon degassed. ^cMaximum of fluorescence band. ^dFluorescence quantum yields measured by using quinine sulfate monohydrate as a standard. ^eFluorescence decay lifetimes.

chromophore in **PPEM2** has essentially the same $\pi \rightarrow \pi^*$ energy band structures as in **MC1**. The absorption spectrum of **PPEP1** is red-shifted by 40 nm compared to **PPEM2**, due to the smaller conjugation length of **PPEM2**. Based on these results, the **4-L** oligomers are expected to have higher energy emission bands, with the spectra of the **4-L** series being significantly blue-shifted from the **5-L** and **5-LP** oligomers.

The fluorescence lifetimes of polymers **PPEM1** and **PPEM2** are expected to be longer than polymers **PPEP1** and **PPEP2**. The shorter lifetimes for the para linked polymers results from the increased excited state delocalization throughout the polymer backbone. This increased delocalization raises the radiative decay rate, and in turn shortens the fluorescence lifetime. The opposite situation arises for the meta linked polymers, where the less delocalized excited state results in a lower radiative decay rate, which increases the fluorescence lifetime. Swager's work clearly shows this, where the lifetime of **PPEM1** is nearly twice that of **PPEP1** (Table 5.3). By decreasing the radiative decay rate, a decrease in the quantum yields for **PPEM1** and **PPEM2** is expected, which is clearly seen throughout the series (Table 5.3). In the **4-L** oligomers, this allows us to predict that the fluorescence lifetimes will be longer than the **5-L** and **5-LP** series, along with a lower quantum yield relative to the **5-L** and **5-LP** oligomers.

Regrettably due to the lack of work with transition metal doped meta linked PPE polymers, we can only use the previous gained knowledge on the all organic PPE based polymers to predict the optical properties of the **4-Re** complexes. The absorption spectra of the **4-Re** complexes are expected to be

blue-shifted relative to the **5-Re** and **5-ReP** series. This is reasonable to assume since the conjugation break incorporated into the **4-L** oligomers is still present in the **4-Re** complexes. In the **5-Re** and **5-ReP** complexes the red-shifted low energy absorption band is composed of the “central” metal chromophore while in the **4-Re** series, the “central” metal chromophore is perturbed due to the meta linkage in the bipyridine ring, leading to a shorter conjugation length relative to the **5-Re** compounds. Although the conjugation is disturbed by the meta substitution, metallation should induce a red-shift in the absorption spectra due to two reasons. First, the pyridine rings after metallation are forced into a cisoid conformation, allowing for stronger electronic communication within the bipyridine ring relative to the unmetallated oligomer. Second, by placing an electropositive metal within the backbone of the oligomer, it is expected that the energy of the π, π^* transition will be slightly lowered due to electrostatic effects. The most interesting point of the **4-Re** work relates to the relative energies of the intra-ligand triplet and MLCT states. Placement of the organic “ligand” in line with the transition dipole of the MLCT transition is expected to have a drastic effect on the complex’s photophysics. The effect of enhanced spin-orbit coupling induced by the transition metal might induce phosphorescence from the organic ligand, allowing for better resolution between the two states.

UV-Visible Absorption Spectra

The conjugation length of the **4-L** series is defined very early, similar to the analogous **5-L** oligomers. This is evident in that the π, π^* transition initially shifts from 346 nm for **4-L-1** to 384 nm for **4-L-2** but remains constant for the

larger oligomer **4-L-3**, $\lambda_{\text{max}} = 384 \text{ nm}$. In the **5-L** series this chromophore largely consists of the bipyridine ring extending to the first phenyl of the biphenyl ring, where the lack of planarity of the biphenyl group breaks the conjugation (Figure 5.11). The **4-L** series is very similar, except that the conjugation length is now no longer predominately through the bipyridine ring. The “meta” substitution and the lack of planarity of the bipyridine ring disturbs the conjugation (Figure 5.12). The conjugation length of the **4-L** series is mainly composed of the bipyridine ring extending through the 4-position to the first biphenyl group.

The absorption spectra of the **4-Re** complexes mimics the trends observed for the **4-L** oligomers. The smallest complex **4-Re-1** has a conjugation length

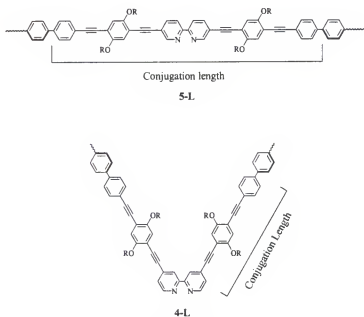


Figure 5.11: The conjugation length of the **5-L** oligomers relative to the **4-L** oligomers.

mainly composed of the bipyridine ring extending out to the first group and has an absorption centered at 378 nm. As the size of the oligomer increases from **4-Re-1** to **4-Re-2** this absorption band moves further out into the red, centered at 408 nm.

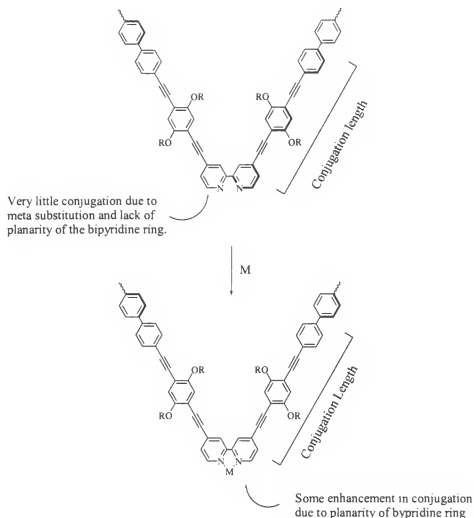


Figure 5.12: Showing the conjugation length of the 4-L oligomers prior to and after metallation.

This is consistent with an increased conjugation length, which is now largely composed of the bipyridine ring extending out to the first phenyl of the biphenyl group. Little to no enhancement in the conjugation length is expected past the first phenyl group of the biphenyl ring. This is proven by the fact that the

absorption maximum for the **4-Re-3** complex exhibits not further red-shifting relative to **4-Re-2**, again indicating a fixed “peripheral” metal chromophore (Figure 5.12). Another factor contributing to the red-shifted absorption band of the **4-Re** complexes is the electrostatic influence induced by incorporation of the transition metal, the exact influence this has is difficult to directly ascertain though. Complex **4-Re-1** exhibits a distinct shoulder (Figure 5.6b) on the red-side of the low-energy π, π^* absorption, this is conclusive evidence of an unobscured MLCT absorption which has been buried under the more intense π, π^* absorptions of the larger oligomers. Is it interesting to note that the **4-Re** complex’s low-energy absorption band continues to increase in intensity with increasing oligomer size. This is opposite to the trends observed in the **5-Re** and **5-ReP** series where this transition remains fairly constant throughout the series. This may have to do with the placement of the MLCT transition dipole in line with the organic ligand, which may influence the oscillator strength of the transition, although it is unclear at this time.

Emission Spectra

The emission spectra of the **4-L** series exhibit strong π, π^* fluorescence very similar to that of the **5-L** and **5-LP** series. The emission maxima remain fairly consistent throughout the series, indicating that the energy of the $^1\pi, \pi^*$ state remains constant as the oligomer size increases. The emission maxima for the **5-L** and **5-LP** oligomers are all substantially red-shifted compared to the **4-L** compounds, which is expected due to the higher excited state energy of the absorption bands in the latter compounds. One noticeable difference between the

4-L series and the 5-L and 5-LP oligomers is that phosphorescence was detected for the 4-L-1 and 4-L-2 oligomers (Figure 5.7). This phosphorescence is very similar in band shape and structure to that proposed for the 5-Re and 5-ReP series. The oligomer fluorescence typically red-shifts with decreasing temperature, resulting in a very broad low temperature emission. Along with this red-shift, the fluorescence intensity increases between 298 and 200 K. However, below 190 K a huge fluorescence quenching is observed, followed by the appearance of phosphorescence in the red portion of the spectrum. Oligomer 4-L-2 also exhibits similar fluorescence quenching followed by the appearance of phosphorescence but it occurs at a much lower temperature (160 K) relative to the 4-L-1 oligomer. This intersystem crossing to form the $^3\pi, \pi^*$ is highly efficient in 4-L-1 where nearly all the fluorescence is quenched at low temperature, and moderately efficient for 4-L-2 where substantial quenching is observed. This observation seems to indicate that the competition between nonradiative decay pathways and phosphorescence is dependent on the oligomer size. It appears that in oligomer 4-L-1 that phosphorescence is the most likely decay pathway, while in the 4-L-2 oligomer the larger molecular size allows for competition between nonradiative decay and phosphorescence. This is supported by the fact that the larger oligomer 4-L-3, exhibits no noticeable phosphorescence where it is expected that the nonradiative pathways will dominate due to the increased oligomer size.

The room temperature fluorescence lifetimes for the 4-L oligomers are significantly longer than the 5-L and 5-LP series. This is consistent with a less

conjugated system where the meta linkage decreases the radiative decay rate, raising the lifetimes in the **4-L** series. The quantum yields of the **4-L** oligomers are very high, similar to the **5-L** and **5-LP** oligomers. Measurement of the quantum yields of the **4-L-2** and **4-L-3** proved difficult, failing to yield a consistent number after several attempts. The propensity of these oligomers to aggregate might contribute to the erroneously high numbers.

The emission spectra of the **4-Re** series proved interesting (Figure 5.8). At room temperature the emission spectrum of **4-Re-1** is broad and blue-shifted, and based upon the lifetime (37 ns) is attributed to MLCT based emission. Complex **4-Re-2** exhibits quite different trends relative to **4-Re-1**. First, at room temperature, the spectrum is dominated mainly by MLCT based emission, as seen in Figure 5.8b, but with the noticeable difference from **4-Re-1** that a shoulder exists on the blue side of the emission, centered at 615 nm. Concurrent to a decrease in temperature is the loss of the MLCT based emission followed by the growth of $^3\pi,\pi^*$ phosphorescence centered at 615 nm. This phosphorescence is nearly identical to that observed in the **4-L-2** spectrum, Figure 5.7b. It also is important to note that the band position is temperature independent, again giving support to the assignment as $^3\pi,\pi^*$ phosphorescence. The same transition is not seen in **4-Re-3**, where the structured emission remains at all temperatures. This allows us to conclude that the low temperature spectra of the **4-Re-2** and **4-Re-3** complexes is largely composed of $^3\pi,\pi^*$ phosphorescence from the oligomer backbone, while the room temperature spectra is composed of a mixture of $^3\pi,\pi^*$

phosphorescence and $^3\text{MLCT}$ luminescence. The spectrum of **4-Re-1** is dominated by $^3\text{MLCT}$ luminescence at both low and room temperature.

Conclusion

A new series of oligomers was successfully synthesized and its optical properties thoroughly investigated. In comparing the **5-L** and **4-L** series of oligomers, several similarities and differences were observed. The most notable difference revolved around the effective conjugation length of the oligomers. As predicted, the **4-L** series had substantially blue-shifted absorption spectra relative to the **5-L** series. This blue-shift is attributed to the change of substitution patterns on the 2,2'-bipyridine ring. In the **5-L** and **5-LP** oligomers the para substitution pattern in the bipyridine ring provides for strong electronic communication between the two oligomer segments. In the **4-L** oligomers, the opposite trend is observed, where substitution in the meta position provides for very poor electronic communication between the two organic segments. Instead of having a central conjugation length, as previously described, the conjugation length in the **4-L** series is largely determined by the organic segment expanding out from the bipyridine ring (Figure 5.11). A conjugation enhancement is observed until you reach the first biphenyl group, and significantly drops off after that. This is evident in the fact that the absorption maximum changes only 4 nm between **4-L-2** and **4-L-3**. This significantly shorter conjugation length accounts for the 20 nm blue-shift between the **4-L** and **5-L** oligomers. It is also significant to note that for the first time, phosphorescence was observed in **4-L-1** and **4-L-2** oligomers at reduced temperatures.

For the rhenium complexes, the advantage of the “bent” oligomers revolves around the change in direction of the MLCT transition dipole relative to the π -conjugated system. In the **5-Re** series, the MLCT transition dipole is perpendicular to the conjugated organic segment, leading to a reduction in electronic communication between the metal and the π -conjugated ligand. In the **4-Re** derivatives the transition dipole is directly in line with the conjugated organic segments. The advantage of having the MLCT transition dipole directly in line with the organic segments is that a more efficient mixing of states is observed. By placing the transition metal in communication with the organic ends, an enhancement in spin-orbit coupling is observed. This enhancement in spin-orbit coupling contributed to the **4-Re** photophysics in several ways. First, the **4-Re-1** complex is dominated by metal based transitions, where the predominant deactivation pathway involves $^3\text{MLCT}$ based emission. The triplet energy of the π -system is higher due to the shorter conjugation length at this stage. As the size of the oligomer increases, the triplet energy of the organic ligand decreases, and in turn has a significant effect on the photophysics of **4-Re-2**. At room temperature the photophysics of **4-Re-2** is composed of a mixture of both states, $^3\pi, \pi^*$ phosphorescence from the organic backbone, as well as $^3\text{MLCT}$ based emission. As the temperature decreases, a loss in $^3\text{MLCT}$ based emission is observed as well as an enhancement in $^3\pi, \pi^*$ phosphorescence. This is expected in that as the temperature decreases, the energy of the $^3\text{MLCT}$ is slightly raised, due to solvent reorganization effects, making phosphorescence the predominant pathway for deactivation. Similar trends for **4-Re-3** were observed, where again

$^3\pi,\pi^*$ phosphorescence is the major decay pathway at low temperature, along with a mixture of both states at room temperature.

Experimental

Photophysical Measurements

All sample solutions studied are either in THF or 2-MTHF (2-methyl-tetrahydrofuran) solutions. All photophysical studies were conducted in 1 cm quartz cuvettes. All room temperature studies were conducted on Argon bubble degassed solutions, and all low temperature studies were conducted on solvent glasses degassed by four freeze-pump-thaw cycles (ca. 10^{-4} Torr). For the absorption and emission studies, sample concentrations were adjusted to produce optically dilute solutions (i.e., $A < 0.20$ at all wavelengths).

Absorption spectra were collected on either an HP8452A diode-array or Varian Cary 100 dual-beam spectrometer. Corrected steady state emission measurements were conducted on a SPEX F-112 fluorimeter. Emission quantum yields were measured relative to 9,10-dicyanoanthracene ($\Phi_{em} = 0.89$) and perylene ($\Phi_{em} = 0.89$) in ethanol [40]. Time-resolved emission decays were observed with time-correlated single photon counting (FLT, Photochemical Research Associates; Excitation filter/source: Schott UG-11/H₂ spark (350 nm maximum) or 405 nm IBH NanoLED-07 laser diode; Emission filter 450 and 550 nm (**4-L** oligomers) or 600 nm (**4-Re** complexes) interference filters). Lifetimes were determined by the observed decays with DECAN fluorescence lifetime deconvolution software [73]. Low temperature emission measurements were

conducted in 1 cm glass tubes contained in an Oxford Instruments cryostat connected to an Omega CYC3200 automatic temperature controller.

General Synthetic

Diisopropylamine was distilled from KOH and tetrahydrofuran was distilled from sodium benzophenone ketyl and stored under argon. The synthesis of 2-iodo-1,4-dimethoxybenzene [74], and 2-iodo-1,4-dioctadecyloxybenzene [74] is described elsewhere. Copper (I) iodide, $\text{Pd(PPh}_3)_2\text{Cl}_2$, $\text{Pd(PPh}_3)_4$ were purchased from Aldrich Chemical Co. and used without further purification. Trimethylsilylacetylene and 2-methyl-3-butyne-2-ol were obtained from GFS chemicals and used without further purification. All cross-coupling reactions using $\text{Pd(PPh}_3)_2\text{Cl}_2$ and $\text{Pd(PPh}_3)_4$ were carried out under standard Schlenk and vacuum line techniques.

Synthesis

2,2'-Bipyridyl-1,1'-dioxide (36)

2,2'-Bipyridine (6.5 g, 0.040 mol) was dissolved in 30 mL of glacial acetic acid and the solution was slowly heated to 50°C. A 30% solution of H_2O_2 (30 mL) was added over a period of ten minutes by means of an addition funnel. The solution was heated for 24 hr, at which time the solution changed from a clear color to a bright yellow color. The acetic acid was removed under vacuum with heating leaving a crude yellow solid. This solid was then recrystallized in acetonitrile to yield a white powder, 6.65 g (85%).

^1H NMR (300 MHz, D_2O) δ 8.30 (d, 2H), 7.66 (d, 2H), 7.58 (m, 4H).

4,4'-Dinitro-2,2'-bipyridyl-1,1'-dioxide (37)

Compound **36** (1.13 g, 0.006 mol) was dissolved in 4.8 mL of H_2SO_4 and placed in a three-neck 25 mL round bottom flask. The solution was cooled to 0°C in an ice bath. After the solution was cooled, 1.9 mL of fuming nitric acid was added and the solution was heated to reflux for 15 hr, making certain to keep the reaction under positive nitrogen pressure. The solution went from a light yellow color to a dark red color near the end of the reaction. The solution was cooled to room temperature and dropped into 15 g of ice. The yellow precipitate was collected via a coarse frit and rinsed with a 25 mL of an aqueous 20% Na_2CO_3 solution, 0.504 g (30 %). ^1H NMR (300 MHz, DMSO) δ 8.65 (d, 2H), 8.56 (d, 2H), 8.36 (dd, 2H).

4,4'-Dibromo-2,2'-bipyridine-1,1'-dioxide (**38**)

Compound **37** (2.38 g, 0.0085 mol) was dissolved in 36 mL of acetic acid and heated to 60°C in a three neck round bottom flask. Acetyl bromide (18 mL) was then slowly added dropwise via an addition funnel. The solution turned from a pale yellow color to a slightly orange color near the end of the addition process. The solution was then heated to 100°C for 4 hr and then allowed to cool to room temperature. The cooled solution was then dropped onto 100 g of ice and this solution was then neutralized with a 100 mL of a 2M NaOH solution. The aqueous layer was then extracted with chloroform (5 x 100 mL) and the chloroform extractions were dried over Na_2SO_4 and removed under reduced pressure, yielding a yellow solid. Due to the instability of **38**, it was used without further purification, 1.17 g (40 %). ^1H NMR (300 MHz, CDCl_3) δ 8.26 (d, 2H), 8.00 (s, 2H), 7.77 (dd, 2H).

4,4'-Dibromo-2,2'-bipyridine (39)

Compound **38** (1.0 g, 2.29 mmol) was dissolved in 25 mL of chloroform and placed in a 3-neck round bottom flask and cooled to 0° C in an ice bath. To this solution was added PBr₃ (4.0 mL, 0.042 mol) dropwise over a period of 5 minutes. The solution was then heated to reflux for 3 hr, cooled and poured onto 100 g of ice. This solution was then quenched with 150 mL of a 2M NaOH solution, and extracted with 3 x 50 mL portions of chloroform. The chloroform extractions were dried over Na₂SO₄ and removed under reduced pressure, yielding a white powdery solid, 0.750 g (82 %).

¹H NMR (300 MHz, CDCl₃) δ 8.60 (s, 2H), 8.48 (d, 2H), 7.50 (dd, 2H).

4,4'-Bis(trimethylsilylethynyl)-2,2'-bipyridine (40)

To a solution of 4,4'-dibromo-2,2'-bipyridine (1.1 g, 3.50 mmol) in triethylamine (40 mL) and acetonitrile (5 mL) under argon was added Pd(PPh₃)₄ (0.450 g, 0.350 mmol) and CuI (0.067 g, 0.350 mmol). Following the addition, trimethylsilylacetylene (1.0 g, 8.4 mmol) was added. The mixture was heated at 60° C for 24 h. The solvents were removed under reduced pressure, and the crude brown solid was chromatographed on silica gel with ethyl acetate/hexane as eluent (4:1) to give 0.680 g of a tan solid, compound **40**, R_f = 0.2 (75%). ¹H NMR (300 MHz, CDCl₃) δ 8.58 (d, 2H), 8.39 (s, 2H), 7.27 (dd, 2H), 0.24 (s, 18H). ¹³C-NMR (75.4 MHz, CDCl₃) δ 155.4, 149.0, 132.2, 125.6, 123.5, 102.1, 99.9, 0.35.

4,4'-Diethynyl-2,2'-bipyridine (41)

Compound **40** (0.470 g, 1.35 mmol) was dissolved in THF (25 mL) and methanol (10 mL) along with 2 mL of water. To this solution was added 3 mL of 4M NaOH and a suspension formed immediately. The solution was stirred at room temperature for 6 hr at which time 25 mL of water was added and the solution was extracted with chloroform. The chloroform was removed under reduced pressure and the white solid was used without further purification, 0.165 g (75%). ^1H NMR (300 MHz, CDCl_3) δ 8.62 (d, 2H), 8.45 (s, 2H), 7.35 (dd, 2H), 3.30 (s, 2H). ^{13}C -NMR (75.4 MHz, CDCl_3) δ 155.6, 149.2, 132.2, 126.1, 123.7, 81.9, 81.0.

Compound 42

4-Ethynylbiphenyl (1.0 g, 0.0056 mol), compound **21** (1.60 g, 0.0056 mol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.117 g, 0.168 mmol) and CuI (0.064 g, 0.336 mmol) were combined in a Schlenk flask and degassed with argon. To this solution was added degassed THF (50 mL) and $(i\text{-Pr})_2\text{NH}$ (30 mL), and the solution was heated at 80°C for 12 hr. The highly fluorescent solution was then cooled and the solvents removed under vacuum. Chromatography on silica gel with 90:10 CHCl_3 /hexane mixture afforded **42** as a tan solid, 1.67 g (40%), $R_f = 0.55$. ^1H -NMR (300 MHz, CDCl_3) δ 7.58 (s, 6H), 7.45 (t, 2H), 7.37 (d, 1H), 6.98 (s, 1H), 6.91 (s, 1H), 3.98 (t, 4H), 2.10 (s, 1H), 1.85 (m, 4H), 1.64 (s, 6H), 1.55 (m, 4H), 1.25 (s, 56 H), 0.88 (t, 6H). ^{13}C -NMR (75.4 MHz, CDCl_3) δ 153.80, 153.6, 140.9, 140.3, 131.9, 128.8, 127.6, 127.0, 122.3, 117.0, 116.6, 113.9, 113.2, 104.4, 99.1, 94.7, 78.5 (overlapping

peak), 69.6, 69.4, 65.8, 32.0, 31.4, 29.7, 26.0, 22.7, 14.2. EI-MS calcd for $C_{61}H_{92}O_3$: 873; found 873.

Compound 43

Compound **42** (0.500 g, 1.50 mmol) was dissolved in 25 mL of toluene and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (0.890 g, 0.015 mmol) was added and the Schlenk tube was immersed for 5 minutes into an oil bath that had been pre-heated to 110° C. The reaction mixture was cooled and then extracted with $CHCl_3$ (2 x 100 mL). Evaporation of the solvent afforded compound **43**, 271 mg (yield 65%). ^1H -NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 6H), 7.45 (t, 2H), 7.37 (d, 1H), 7.02 (s, 1H), 6.98 (s, 1H), 4.02 (t, 4H), 3.35 (s, 1H), 1.85 (m, 4H), 1.55 (m, 4H), 1.25 (s, 56 H), 0.88 (t, 6H). ^{13}C -NMR (75.4 MHz, $CDCl_3$) δ 154.1, 153.4, 140.9, 140.3, 132.0, 128.8, 127.6, 126.9 (overlapping peak), 122.2, 117.7, 116.8, 114.6, 112.4, 94.8, 86.4, 82.3, 80.0, 69.6, 31.9, 29.7, 26.0, 25.8, 22.7, 14.2. EI-MS calcd for $C_{58}H_{86}O_2$: 815; found 815.

Protected Oligomer 44

4,4'-Diethynyl-2,2'-bipyridine (0.150 g, 0.734 mmol), compound **16** (1.53 g, 1.54 mmol), $Pd(PPh_3)_2Cl_2$ (0.031 g, 0.044 mmol) and CuI (0.017 g, 0.088 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (50 mL) and diisopropylamine (30 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 16 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with 80:20 $CHCl_3$ /hexane mixture afforded an orange solid, which eluted off the column as a highly fluorescent orange band, 571 mg (40%), R_f =

0.2. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.66 (dd, 2H), 8.55 (s, 2H), 7.56 (m, 16H), 7.42 (dd, 2H), 7.05 (s, 4H), 4.05 (br t, 8H), 1.88 (br m, 8H), 1.64 (s, 12H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); $^{13}\text{C-NMR}$ (75.4 MHz, CDCl_3) δ 155.7, 153.9, 153.5, 149.1, 140.0, 139.9, 132.6, 132.1, 132.0, 126.8, 126.7, 125.4, 123.1, 122.6, 122.0, 117.0, 116.7, 114.9, 112.8, 95.2, 94.6, 92.3, 90.8, 86.8, 81.9, 69.6, 65.7, 31.5, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; APCI MS calcd for $\text{C}_{136}\text{H}_{189}\text{N}_2\text{O}_6 [\text{M}+\text{H}^+]$: 1946.5; found 1946.5.

Oligomer 44

Protected oligomer **44** (300 mg, 0.154 mmol) was dissolved in 10 mL of toluene and the solution was thoroughly degassed with argon for 1 hr. Crushed potassium hydroxide (138 mg, 2.46 mmol) was added and the Schlenk tube was immersed for 5 minutes into an oil bath that had been pre-heated to 110° C. The reaction mixture was cooled and then extracted with CHCl_3 (2 x 100 mL). Evaporation of the solvent afforded compound **44**, yield 281 mg (71%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 8.66 (dd, 2H), 8.55 (s, 2H), 7.62 (s, 16H), 7.42 (dd, 2H), 7.05 (s, 4H), 4.05 (br t, 8H), 3.18 (s, 2H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H).

Oligomer 4-L-1

2-Iodo-1,4-dioctadecyloxybenzene [51] (1.4 g, 1.83 mmol), 4,4'-diethynyl-2,2'-bipyridine (0.150 g, 0.734 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.031 g, 0.044 mmol) and CuI (0.017 g, 0.088 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (30 mL) and diisopropylamine (20 mL) was added to the Schlenk flask and the resulting

solution was heated at 80° C for 14 hr. The solution was cooled and the solvents removed under vacuum. Chromatography on silica gel with a 70:30

CHCl₃/hexane mixture afforded **4-L-1** as a white solid, 524 mg (50%), $R_f = 0.45$.

¹H NMR (CDCl₃) δ 8.66 (d, 2H), 8.53 (s, 2H), 7.40 (d, 2H), 7.03 (d, 2H), 6.88 (m, 4H), 4.03 (t, 4H), 3.95 (t, 4H), 1.85 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); ¹³C NMR (CDCl₃) δ 155.6, 154.4, 152.7, 149.0, 132.8, 125.4, 123.1, 118.4, 117.7, 113.9, 112.4, 90.9, 90.7, 69.7, 68.7, 31.9, 29.7, 29.3, 26.1, 25.9, 22.7, 14.1; APCI MS calcd for C₉₈H₁₆₁N₂O₄ [M+H⁺]: 1430.3; found 1430.3.

Oligomer 4-L-2

Compound **42** (0.200 g, 0.245 mmol), 4,4'-Dibromo-2,2'-bipyridine (0.036 g, 0.12 mmol), Pd(PPh₃)₂Cl₂ (0.010 g, 0.015 mmol) and CuI (0.006 g, 0.029 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (20 mL) and diisopropylamine (10 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 16 hr. The solution was cooled and the solvents removed under vacuum.

Chromatography on silica gel with an 80:20 CHCl₃/hexane mixture afforded **4-L-2** as a yellow solid, the product eluting off as a highly fluorescent yellow band, 110 mg (52%), $R_f = 0.50$. ¹H-NMR (300 MHz, CDCl₃) δ 8.67 (d, 2H), 8.55 (s, 2H), 7.62 (s, 12H), 7.46 (m, 8H), 7.06 (br s, 4H), 4.06 (t, 4H), 1.88 (br m, 4H), 1.50 (br m, 4H), 1.23 (br s, 56H), 0.88 (br t, 6H); ¹³C-NMR (75.4 MHz, CDCl₃) δ 155.6, 154.0, 153.5, 149.1, 141.0, 140.3, 132.8, 132.0, 128.8, 127.6, 127.0, 126.9, 125.4, 123.1, 122.2, 117.0, 116.7, 115.0, 112.6, 95.3, 92.2, 90.8, 86.5, 69.6,

31.9, 29.7, 29.4, 26.1, 26.0, 22.7, 14.1; APCI MS calc'd for $C_{126}H_{177}N_2O_4$

$[M+H]^+$: 1782.4; found 1782.4.

Oligomer 4-L-3

Oligomer **44** (0.200 g, 0.109 mmol), 2-iodo-1,4-dimethoxybenzene [51] (0.143 g, 0.545 mmol), $Pd(PPh_3)_2Cl_2$ (0.005 g, 0.0065 mmol) and CuI (0.003 g, 0.013 mmol) were combined in a Schlenk flask which was then degassed with argon. A degassed mixture of THF (20 mL) and diisopropylamine (10 mL) was added to the Schlenk flask and the resulting solution was heated at 80° C for 8 hr. The solution was cooled and the solvents removed under vacuum.

Chromatography on silica gel with a 80:20 $CHCl_3$ /hexane mixture afforded **4-L-3** as a flaky yellow solid, the product eluting off as a highly fluorescent yellow/orange band, 183 mg (80%), $R_f = 0.6$. ^1H -NMR (300 MHz, $CDCl_3$) δ 8.75 (d, 2H), 8.55 (s, 2H), 7.62 (s, 16H), 7.42 (dd, 2H), 7.06 (br s, 6H), 6.86 (br d, 4H), 4.06 (br t, 8H), 3.89 (s, 6H), 3.79 (s, 6H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); ^{13}C -NMR (75.4 MHz, $CDCl_3$) δ 155.7, 154.5, 153.9, 153.6, 153.2, 149.1, 140.1, 139.8, 132.6, 132.2, 132.0, 126.8, 126.7, 125.4, 123.1, 122.7, 122.6, 118.0, 117.0, 116.8, 115.8, 115.0, 112.8, 112.7, 112.0, 95.2, 93.2, 92.3, 90.8, 86.8, 86.7, 69.6, 69.5, 56.5, 55.7, 31.9, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; APCI MS calcd for $C_{146}H_{193}N_2O_8$ $[M+H]^+$: 2102.5; found 2102.5.

Metal-Organic Oligomer 4-Re-1

Oligomer **4-L-1** (0.100 g, 0.069 mmol) and $Re(CO)_5Cl$ (0.030 g, 0.082 mmol) were dissolved in 30 mL of toluene and the solution was purged with

argon and subsequently heated at 90°C for 2 hr. The solution color changed from light orange to deep red. During the course of the reaction the blue-green fluorescence characteristic of oligomer **4-L-1** disappeared. The solution was cooled and the toluene removed under vacuum, affording **4-Re-1** as a red/orange solid. The complex was purified by repeated rinsing with acetone, 97 mg (82%). ¹H-NMR (300 MHz, CDCl₃) δ 8.97 (d, 2H), 8.20 (s, 2H), 7.52 (d, 2H), 7.04 (d, 2H), 6.96 (dd, 2H), 6.87 (s, 1H), 6.85 (s, 1H), 4.03 (br t, 4H), 3.93 (t, 4H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); ¹³C-NMR (75.4 MHz, CDCl₃) δ 197.0 (CO), 189.3 (CO), 155.3, 154.8, 152.7 (overlapping), 135.4, 128.5, 124.7, 118.9, 118.5, 113.6, 110.8, 96.8, 89.0, 69.4, 68.7, 31.9, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; IR (KBr) 2926, 2854, 2205, 2026, 1928, 1902, 1600, 1502, 1466, 1417 cm⁻¹.

Metal-Organic Oligomer **4-Re-2**

Oligomer **4-L-2** (0.050 g, 0.028 mmol) and Re(CO)₅Cl (0.012 g, 0.033 mmol) was dissolved in 10 mL of toluene and the solution was purged with argon and subsequently heated at 90°C for 2 hr. The solution color changed from light orange to deep red. During the course of the reaction the blue-green fluorescence characteristic of oligomer **4-L-2** disappeared. The solution was cooled and the toluene removed under vacuum, affording **4-Re-2** as a brick red solid. The complex was purified by repeated rinsing with acetone, 51 mg (88%). ¹H-NMR (300 MHz, CDCl₃) δ 8.99 (d, 2H), 8.19 (s, 2H), 7.62 (br s, 12H), 7.46 (m, 8H), 7.06 (br s, 4H), 4.06 (br t, 8H), 1.88 (br m, 4H), 1.50 (br m, 4H), 1.23 (br s, 56H), 0.88 (br t, 6H). ¹³C-NMR (75.4 MHz, CDCl₃) δ 196.9 (CO), 189.2 (CO), 155.3,

154.4, 153.5, 152.7, 141.2, 140.2, 140.0, 135.1, 132.0, 128.8, 127.7, 127.0, 126.9, 124.7, 121.9, 116.8, 116.7, 116.5, 110.8, 96.7, 96.2, 90.4, 86.2, 69.7, 69.4, 31.9, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; IR (KBr) 2926, 2854, 2205, 2024, 1928, 1901, 1600, 1502, 1466, 1417 cm^{-1} .

Metal-Organic Oligomer 4-Re-3

Oligomer **4-L-3** (0.100 g, 0.048 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ (0.021 g, 0.057 mmol) were dissolved in 30 mL of toluene and the solution was purged with argon and subsequently heated at 90° C for 2 hr. The solution color changed from light orange to deep red. During the course of the reaction the blue-green fluorescence characteristic of oligomer **4-L-3** disappeared. The solution was cooled and the toluene removed under vacuum, affording **4-Re-3** as a brick red solid. The complex was purified by repeated rinsing with acetone, 107 mg (96%). ^1H -NMR (300 MHz, CDCl_3) δ 8.97 (d, 2H), 8.19 (s, 2H), 7.62 (br s, 16H), 7.54 (dd, 2H), 7.06 (br s, 6H), 6.83 (br d, 4H), 4.06 (br t, 8H), 3.89 (s, 6H), 3.79 (s, 6H), 1.88 (br m, 8H), 1.58 (br m, 8H), 1.23 (br s, 112H), 0.88 (br t, 12H); ^{13}C -NMR (75.4 MHz, CDCl_3) δ 196.9 (CO), 189.2 (CO), 155.3, 154.4, 153.5, 153.2, 152.7, 140.3, 139.7, 135.0, 132.2, 132.1, 130.8, 128.7, 128.5, 126.8, 126.7, 124.7, 122.8, 122.3, 118.0, 116.8, 116.6, 115.8, 112.8, 112.0, 110.9, 96.7, 96.1, 93.1, 90.4, 86.7, 86.5, 69.6, 69.4, 56.4, 55.7, 31.9, 29.7, 29.3, 26.1, 26.0, 22.7, 14.1; IR (KBr) 2926, 2854, 2205, 2024, 1928, 1901, 1600, 1502, 1466, 1417 cm^{-1} .

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BIOGRAPHICAL SKETCH

I was born on June 12, 1974, in Aliquippa, Pennsylvania, to James and Joanne Ley as the third child in a family of five. As a child my youth was fulfilled with the typical joys that every child should have, good friends, sports, and most importantly family. At the age of eleven I moved to Florida, and happily enjoyed the warm sunny beaches of the Gulf Coast. I attended Florida State University for my undergraduate work, and participated in undergraduate research with Professor Edwin Hilinski. After graduation, I joined the research group of Professor K. Schanze at the Department of Chemistry at the University of Florida for my graduate studies.

After my final defense, I will be joining QTL biosystems in Santa Fe, New Mexico, as a research and development chemist.

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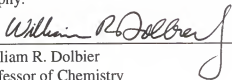
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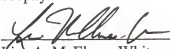
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December, 2000

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